

STANDARD OPERATING PROCEDURES MANUAL
FOR THE
DEPARTMENT OF ENVIRONMENTAL QUALITY
OFFICE OF WATER QUALITY MONITORING AND ASSESSMENT

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Introduction to Water Quality Assessments Operating Procedures Manual

This document describes the routine operations and quality control activities performed by the Department of Environmental Quality (DEQ) in most of its ongoing data generating programs. Outlining procedures for sampling and field testing activities helps ensure that these procedures are standardized geographically across the state and between monitoring programs. The procedures described in this manual also help ensure that sampling precision, accuracy, representativeness, comparability and completeness of the data are obtained and documented. The sample collection procedures described in this document must be followed for all Water Quality Monitoring Programs unless the program is specifically covered under another SOP and/or Quality Assurance Project Plan that has been approved by the agency's QA officer.

Many of the DEQ water quality monitoring programs have similar sample collection, field testing activities, and quality assurance requirements. Data generated from these programs must meet the needs of the data users. Comparability of data between DEQ's sampling programs and regional offices is an important quality objective.

TABLE OF CONTENTS

Section I. Sampling Requirements	6
A) Sampling Equipment	6
a) Grab Sampling Equipment	6
a.1) Water Matrices	6
a.2) Sediment Matrices	6
B) Sampling Equipment Preparation and Cleaning	6
b.1) Aqueous Sampling Equipment	6
b.2) Sediment Sampling Equipment	6
C) Sample Containers, Handling, and Preservation	7
D) Sample Container Handling and Storage	7
E) Chemical preservatives and reagents	7
Section II: Field Sampling Procedures	9
A) General:	9
a.1) Use of Protective Gloves	9
B) Equipment Rinse	9
Surface Water Sampling	9
General	9
C) Sampling from a Bridge	10
E) Sampling from a Boat (Pump and hose method)	11
D) Streambank and instream sampling	12
d.6) Collection of samples for Chlorophyll a	12
F) Sediment Sampling	13
f.1) Containers	13
f.2) Requirements for equipment	13
f.3) Sampling Preparation	13
f.4) Sampling Collection Protocols	13
f.4.1) General:	13
f. 4.2) Collection with a scoop or jar:	14
f 4.3) Collection with a Core Tube	14
f.4.4) Boat and Bridge sampling	15
Section III: Field Quality Control Samples	17
A) Field Quality Control Samples for Water Matrix	17
a) Equipment Blanks	17
b) Field Duplicate Samples	17
B) Quality Control Requirements for Sediments	18
a) Equipment Blanks	18
b) Duplicate samples	18
Section IV: Field Testing Procedures	19
Accument AP Series Handheld pH/mV/Ion Meter	19
1. General Procedures and Precautions	19
2. Instrument Setup	19
3. Instrument Calibration	20
4. Field Measurement Procedures	21
5. QC limits	21
6. Preventative Maintenance	21
6.1 Battery Requirements	21
6.2 Replacing Batteries	21
6.3 Instrument Electronics Check	22
6.4 pH Electrode Rejuvenation	22
7. Spare Parts and Supplies	23
YSI Model 58 Dissolved Oxygen and Temperature Meter	23
A) Instrument Check	23
B) Daily Calibration	24
a) Air Calibration (% Saturation)	24
b) Air Saturated Water Calibration	25
C) Field Measurement Procedures	25
D) Maintenance	26
a) Field Probe Maintenance	26
b) Probe Performance Checks	26
c) Probe Service	27

E) Quality Control.....	27
E.1) DO meter Calibration Checks	27
E.2) Temperature Calibration Check	28
YSI Model 85 Handheld Oxygen, Conductivity, Salinity, and Temperature System	28
A) Preparing the Probe.....	28
a) Membrane installation	29
B) Calibration	29
a) Calibration of Dissolved Oxygen.....	29
b) Calibration of Conductivity	29
C) Taking Measurements.....	30
D) Quality Control.....	31
D.1) DO and Conductivity meter Calibration Checks	31
D.2) Temperature Calibration Check.....	31
Hydrolab H2O Water Quality Multiprobe with Display.....	31
A) System Components	31
B) Calibration of Parameters.....	32
C) Dissolved Oxygen.....	33
D) Specific Conductance	34
E) pH.....	34
E.2) Temperature Calibration Check	35
F) Depth	36
G) Hydrolab field set-up and operation	36
H) Preparation for use.....	36
I) Field Set-up and Operation.....	37
J) Hydrolab Postcalibration.....	38
a) Dissolved Oxygen.....	38
b) Specific Conductance	38
c) pH	39
K) Preparation of KCL Standards.....	39
K.1) Preparation of 1 Molar KCL stock solution:.....	39
L) Maintenance	40
L.1) Dissolved oxygen.....	40
L.2) Conductivity.....	41
L.3) pH Electrode.....	41
L.4) pH reference electrode maintenance	42
L.5) Temperature Sensor.....	42
Hydrolab Data Sonde and Minisonde Multiprobe with Surveyor.....	42
A) Calibration of Parameters	42
d) Temperature Calibration Check	45
Quanta.....	46
YSI 6000UPG Multi-Parameter Water Quality Monitor	48
In-Situ Multi-parameter Troll 9000 with Pocket Situ	55
D) Profiling	58
E) Logging profiler data	58
G) Postcheck Calibration	58
H) Maintenance.....	59
Section V: Dissolved Oxygen Method (Winkler Azide Modification Titration).....	62
A) Applicability:	62
B) Summary of method:.....	62
C) Health and Safety Warnings:	62
D) Cautions	62
E) Interference:	62
F) Apparatus and Material:	63
G) Instrument or Method Calibration	63
H) Sample Collection:.....	63
a) Collecting a Winkler sample via the Pump and hose procedure:.....	63
b) Collecting Winkler samples via the bucket procedure.....	64
I) Handling and Preservation	64
J) Sample Bottle Cleaning:	64
K) Sample Analysis:	65
L) Data Calculation:.....	65

M) Data Management and Record Management	65
N) Quality Control and Quality Assurance	65
O) Reference:	66
Section VI: Sample Identification and Corrective Action	67
A) Field Data Sheet:	67
B) Sample label and tag	67
C) Corrective Action	67
Appendix A.....Calibration Logsheet	69
Appendix B.....Saturated Dissolved Oxygen Chart	70
Appendix C.....Corrective Action Request Form	71
Appendix D.....Entering QA/QC into CEDS	72
Appendix E.....Miscellaneous Special Sampling Procedures	74

Section I. Sampling Requirements

A) Sampling Equipment

Sampling equipment has specific-cleaning requirements based on its use in the field. Non-metallic materials such as plastic or teflon are used whenever possible for the collection of samples for metals. For the collection of organic samples, non-organic or inert materials such as stainless steel or teflon are used.

Never store or carry the spool in the bucket. Examine the equipment for obvious signs of dirt, rust or scratches and replace when necessary.

a) Grab Sampling Equipment

a.1) Water Matrices

- 1) Rope on spool
- 2) An appropriately sized stainless steel bucket with a fitting for the bacteria sample bottle mounted on the inside, or as a substitute a suitable water sampling device (Van Dorn, Kemmerer, Labline, pump and hose or HDPE Nalgene bottle etc.)
- 3) Syringe, filter paper, filter holder etc.

a.2) Sediment Matrices

- 1) Rope on spool
- 2) Certified pre-cleaned glass jar with Teflon-lined lid
- 3) Teflon coated or plastic spoon, and stainless steel spoon
- 4) Core tube or appropriate dredge (such as Petit Ponar) depending on sediment type and depth of water.
- 5) Appropriately sized stainless steel or plastic pan

B) Sampling Equipment Preparation and Cleaning

b.1) Aqueous Sampling Equipment

- 1) Rinse stainless steel sampling buckets at the end of the sampling day with analyte free water. If using a pump and hose apparatus, follow Chesapeake Bay Program protocols (SOP available in the special project screen in CEDS2000) for pre and post cruise preparations for that apparatus. If using a Kemmerer or Alpha Bottle sampling device follow the manufacturer's recommendations for preparing those sampling devices. Wash sampling buckets with lab grade soap (Liquinox or equivalent) at the end of each week using a brush, if necessary, to remove particulate matter or surface film.
- 2) Rinse thoroughly with tap water and allow to air dry at room temperature.

b.2) Sediment Sampling Equipment

- 1) Soak in lab grade soap and tap water and scrub with a brush.
- 2) Rinse thoroughly with tap water.
- 3) Rinse with reagent grade diluted (10% V: V) hydrochloric acid (add 10 ml of concentrated acid to 90 ml of analyte free water) or reagent grade nitric acid (10% nitric acid is prepared by mixing one part concentrated nitric acid with five parts analyte free water) to remove scale, metals and bases. Do not acid rinse stainless steel equipment.
- 4) Rinse thoroughly with analyte free water.
- 5) Rinse with full strength acetone to remove organic compounds.

- 6) Rinse thoroughly with analyte free water.
- 7) Dry equipment at room temperature in contaminant free air.
- 8) Visually inspect equipment for any contamination prior to storage.
- 9) Cover the clean equipment with clean aluminum foil for organic analysis or plastic wrap for metal analysis.

C) Sample Containers, Handling, and Preservation

- 1) Proper sample containers and sample preservation are essential to sample integrity and representativeness. Refer to the DCLS laboratory catalog in CEDS for the appropriate preservation procedures.
- 2) Check sample container lids to ensure they are tight enough to prevent contamination from water seepage.
- 3) In the field samples should be iced to 4°C in a cooler immediately after collection. In the cooler, samples shall be placed upright and if possible covered with ice to the neck of the sample jar. Bacteria sample bottles and Chlorophyll filter samples will be placed in appropriately sized Ziplock bags and placed on top of the layer of ice. Ziplock bags containing filters should be oriented such that the opening of the Ziplock bag hangs outside the cooler lid when the lid is closed.
- 4) Prior to shipping the containers to the lab, completely drain the water from the coolers and cover the sample containers with ice such that the container openings are above the level of ice.
- 5) Glass samples should first be packed in bubble wrap or other protective material to minimize accidental breakage.
- 6) DCLS provides temperature bottles that they use to determine sample temperature upon arrival to DCLS. Make sure every cooler that will ship samples to DCLS contains one of these bottles.

D) Sample Container Handling and Storage

- 1) Containers purchased by DEQ are parameter and program specific to meet agency and DCLS requirements for sample size and purity, and container construction and material.
- 2) Each case of sample containers should be inspected and any torn, punctured or cracked sample containers discarded.
- 3) Boxes or packages storing sample containers should be dated by the regional office upon receipt and stocked on shelves with the oldest dated box/packages being used first.

E) Chemical preservatives and reagents

General requirements

- 1) Appropriate chemicals for equipment cleaning, and sample preservation are essential to sample integrity and accuracy.
- 2) ACS reagent grade preservatives are required for sample preservation.
- 3) Chemicals should be dated by the regional office upon receipt and upon opening of the container.

f.4.5.4) Waste Disposal

- 1) Decontamination wastes must be segregated and disposed of properly.
- 2) Soap solutions and waste tap/DI/analyte-free water can be poured down the drain.
- 3) Solvents and weak acids used in cleaning may be diluted with water and poured down the sanitary sewer drain.
- 4) Other waste solvents and concentrated, reagent grade preservative acids shall be handled as hazardous waste and must be collected and disposed of properly.

Section II: Field Sampling Procedures

A) General:

The section below details the collection of water and sediment samples utilized by almost all of the water quality monitoring programs. Further collection procedures for some miscellaneous specialty samples (e.g. VOCs, PAHs etc.) can be found in Appendix E.

a.1) Use of Protective Gloves

- 1) Gloves serve a dual purpose: 1) protecting the sample collector from potential exposure to sample constituents and 2) minimizing accidental contamination of samples by the collector.
- 2) Wearing protective gloves at all times while sampling is recommended, however, their use is not mandatory if: 1) the sample source is considered to be non-hazardous, or, 2) the samples will not be analyzed for trace (i.e. part per billion level) constituents.
- 3) Latex or nitrile gloves may be used for common sampling conditions. The use of new, disposable, powder-free latex or nitrile gloves is required for clean metal sampling. Gloves should be changed and discarded after every sampling site. Discarding the gloves is optional but in no circumstances should the gloves be reused for trace analysis sampling.

B) Equipment Rinse

When collecting aqueous samples, the sample collection equipment shall be rinsed once with sample water before the actual sample is taken.

Surface Water Sampling

General

- 1) Safety always comes first. All sampling should be conducted with the proper equipment and least amount of danger to field personnel. Use of safety cones and vests is recommended.
- 2) Site access will be left up to the sampling staff.
- 3) Care should be taken not to disturb the bottom when sampling.
- 4) If water samples and sediment samples are to be taken from the same area, the water samples must be taken first.
- 5) Surface water should always be collected facing upstream and in the main area of flow. Therefore, unless safety is an issue samples should be obtained from a bridge or instream.
- 6) Wherever possible field measurements should be made in situ.
- 7) If utilizing discrete sampling bottles follow the manufacturer's instructions for maintenance, cleaning and use.

8) When collecting bacterial samples:

- a. Do not rinse the bacteria sample bottle before collecting the sample.
 - b. Samples shall never be collected in an unsterilized sample container and transferred to a sterile container.
 - c. Be careful not to insert fingers into the mouth of the container or on the interior of the cap. Bacteriological sampling must always be collected as a grab sample and must never be composited.
- 8) When there are obvious standing pools of water during low or no flow conditions do not collect samples or field measurements.

C) Sampling from a Bridge

d.1) General:

- 1) Sample in the main flow from the safest side of the bridge and where contamination is least likely to occur.
- 2) During rainy periods, avoid sampling where storm water runoff from the bridge can affect sample.
- 3) Field parameters should be obtained immediately.
- 4) In situations where field parameters are obtained from the bucket all water samples must be collected prior to inserting the probe in the bucket.

d.2) Collection of samples with a Stainless Steel Bucket that has been modified for collection of Bacteria samples.

- 1) Lower the bucket into the main flow facing toward the current and carefully rinse the bucket with ambient water 1-2 times. Raise the bucket after rinsing.
- 2) Remove the cap on the bacteria sample bottle, and place the bottle into the rubber tubing on the inside of the bucket.
- 3) Place the rope through the temporary clip located on the side of the bucket.
- 4) Slowly lower the bucket into the main flow. Once sufficient sample has been obtained, jerk the rope to free the rope from the clip and pull the bucket up toward you. The bacteria sample bottle will fill sufficiently.
- 5) Remove the bacteria sample bottle from the rubber tubing and cap it. **Do not pour additional sample into the bacteria sample bottle or dip the bacteria sample bottle into the bucket to increase the volume of the sample.**
- 6) If the volume of sample exceeds the mark on the bacteria sample bottle, pour off sufficient sample so the volume is approximately equal to or above the mark on the bottle shoulder, securely cap and label the container .
- 7) If a chlorophyll sample will be collected follow the steps described in Section d.6 prior to collecting any further samples.

- 7) Pour the samples directly from the bucket into any additional containers to be collected and cap them. Do not fill the containers fully, leave approximately one inch of air space in the bottles.

Add appropriate preservation as described in the DCLS catalog in CEDS.

Put the bacteria sample bottles and chlorophyll filters separately into Ziplock bags, close the bags and place them in the cooler on top of the wet ice. Make sure the opening of the bag containing the chlorophyll filter hangs out of the cooler when the cooler lid is closed.

- 8) Place all remaining sample containers into a cooler and place them in wet ice.

E) Sampling from a Boat (Pump and hose method)

- 1) Bacterial samples need to be collected directly from the water, and not from a pump and hose.
- 2) If possible, sample away from the engine into the direction of the current.
- 3) There are two methods that may be utilized to ensure a sufficient volume of water is allowed to flow through the hose to clear it:

a. Air Bubble method:

1. Turn the pump on allowing air to enter the hose.
2. Lower the hose to the appropriate depth for the monitoring program occurring, such as 0.3 m for ambient watershed or lake monitoring samples, and one meter above the bottom, and one meter below the surface for Chesapeake Bay monitoring.
3. Allow sufficient volume to pump through the system to clear the hose by watching to ensure the air bubble leaves the hose and then allowing sufficient water to flow out of the hose to ensure the sample collected consists of water from the desired depth.
4. Collect the samples.

b. Calculation of clearing time:

Calculate the volume of the hose in gallons: $(r/12)^2 * 3.14 * L * 7.48 = V$ where

r = radius (inches) of hose inner diameter

L = length (feet) of hose

V = volume (gallons)

Determine pump capacity (gallons per minute pumped) from the pump specifications.

Calculate time to flush hose: $V/(gpm) = \text{time}$

Gpm = gallons per minute pumped

Time = minutes to flush hose

Multiply the time by 1.25 as a minimum clearing time for the hose.

Note: Each time a new length or diameter of hose or pump is installed, the clearing time needs to be calculated in the following manner to ensure the waiting time is sufficient to clear the hose.

- 4) When sampling close to the surface make sure the hose does not come out of the water and inadvertently pull some surface skim water through the hose.
- 5) Fill individual sample containers via the discharge hose.

6) Follow the appropriate procedures for sample filtration, preservation, labeling and storage as described in SectionC, Sampling Requirements.

D) Streambank and instream sampling

General:

1. If possible wade into the stream to collect the sample.
2. When sampling from the streambank, care should be taken to sample from an area that will most closely represent the entire stream.
3. If all samples are obtained directly from the stream, preservatives, when necessary should be added after obtaining the sample grabs.
4. When residual chlorine may be present, care must be taken to ensure the sodium thiosulfate tablet remains in the bottle for bacterial samples.

Sample collection:

- 1) Collect the bacterial sample directly from the stream.
- 2) Submerge the container; neck first into the water.
- 3) Invert the bottle so the neck is upright and pointing into the water flow.
- 4) Return the filled container quickly to the surface.
- 5) Rinse the bucket with stream water 1-2 times. Fill the bucket and return to shore to fill the remaining containers.
- 6) Follow the appropriate procedures for sample preservation, labeling and storage as described in the SectionC, Sampling Requirements.

d.6) Collection of samples for Chlorophyll a

Collect Chlorophyll a samples by filtering approximately 300 ml of site water (or sufficient volume to produce a visible residue on the filter) through a 150cc polypropylene syringe as follows:

- 1) Load the polysulfone filter holder with a GF/F filter.
- 2) Rinse the 150cc polypropylene syringe with ambient water. Fill the syringe past the 150cc mark (150cc mark is the middle of "Y" on the syringe). Holding the syringe up, tap on the side to eliminate as many air bubbles as possible and push the plunger until the first ridge of the plunger aligns with the middle of "Y" on the syringe.
- 3) Twist the syringe into the filter holder and apply gentle pressure on the plunger until the water has passed through the filter.

- 4) To refill the syringe, carefully detach the filter assembly, fill the syringe past the 150cc mark, displace the bubbles, push the plunger to 150cc mark and continue with the filtration until the desired volume has been processed or until no water will pass through the filter with gentle pressure.
- 5) If at any time the filter becomes clogged due to high concentrations of suspended solids materials, stop the filtration and record the volume filtered on the field data sheet.
- 6) Detach the syringe from the filter assembly, pull the syringe back, reattach the syringe and apply gentle pressure to force out the remaining water in the filter holder.
- 7) Record the volume of the sample water filtered on the sample tag. The volume filtered must also be entered into CEDS.
- 8) Using forceps, carefully remove the filter from its holder and fold it in half so the pigment is inside. Should the filter tear during the removal process, discard the filter and begin again.
- 9) Place the filter in a piece of 3 by 3 inch aluminum foil, fold the aluminum foil into quarters and attach the sample tag with the sample tag wire or a staple or seal the foil using the adhesive label.
- 10) Place the aluminum foil in a Ziplock bag and store the bag in the cooler on top of the wet ice. Make sure the opening of the bag hangs out of the cooler when the lid is lowered.

F) Sediment Sampling

f.1) Containers

- 1) Regional offices must order wide mouth glass jars with Teflon-lined lids. These jars and lids must be QA/QC guaranteed when purchased.
- 2) Regional offices will check cases of jars to ensure the lids are secure. Any jars without lids should not be used.

f.2) Requirements for equipment

Sediment samples should be collected with sampling equipment that will not introduce contaminants into the sample. For instance, when collecting sediment samples for metals, sterilized plastic or Teflon coated materials are required. When collecting sediment samples for organic trace analyses, use stainless steel, or Teflon coated materials.

f.3) Sampling Preparation

A container will be needed in which to place the sediment samples from a station. For metals analyses, a plastic pan must be used. For organic analyses, a stainless steel pan must be used. Examine the equipment for obvious signs of dirt, rust or scratches and replace when necessary.

f.4) Sampling Collection Protocols

f.4.1) General:

- 1) Using a scoop or spoon composed of an appropriate material, or the glass sample jar, collect the top three centimeters of sediment from the streambed.
- 2) Sediment samples are taken via four types of equipment: the sample jar, scoops, corers and dredges.
- 3) Stainless steel equipment shall be used if trace contaminants are to be sampled.
- 4) Collection of sediment should be from a single area of deposition in the sampling stream.
- 5) The sediment samples should be taken from the streambed, not from the riverbank or flood plain.
- 6) Organic compounds adhere to the small particle size fraction and organic portion of sediments, such as soft muck. If you can not get this type of sample, then you should move to a location from which you can get this type of samples. (Note: At approximately \$1200.00 per sample and knowing organic compounds do not adhere to sand we should either not sample for the organic compounds or move to a nearby location where soft muck is present.)
- 7) Samples for analysis should be taken from the top three centimeters of the retrieved sediment sample with a scoop or spoon. The edges of the sampling device should be avoided when taking the sample for analysis.
- 8) Precautions should be taken to minimize loss of fine bottom sediments.
- 9) Large stone, shells, sticks, plant material and other debris should be removed from the sample.

f. 4.2) Collection with a scoop or jar:

- 1) The sampler may wade into the water body to obtain a scooped sample. The sampler must stand facing the direction of flow and approach the location from the downstream direction.
- 2) Precaution must be taken not to disturb the bottom prior to scooping.
- 3) The sample should be scooped in the upstream direction of the flow.
- 4) Using a scoop or jar, collect the top three centimeters of sediment from the streambed.
- 5) After the suspended sediment settles, siphon off as much water as possible without disturbing the sediment collected.
- 6) If sufficient sample volume was not collected by the first scoop or jarful, pour the sediment sample into a dishpan. Continue collections until the required amount of sediment is obtained. The subsample should be homogenized by stirring before removing an aliquot into the sample jar.
- 7) Place the sample jar in the cooler and place it in wet ice.

f 4.3) Collection with a Core Tube

- 1) In wadable streams or in tidal waters that are too deep to use a glass jar or Teflon spoon, a core tube can be used to collect sediments.

- 2) Minimize water displacement when lowering the core tube.
- 3) The core shall be rotated as it is pushed in.
- 4) Rotation should be around its axis do not rock the core back and forth.
- 5) Rotation improves penetration and prevents compaction of the sample as it is pushed to the full length of the core.
- 6) Upon withdrawal from the water surface, a cap shall be placed on the top to prevent the sample from sliding out.
- 7) Place another cap on the sediment end of the core tube as it raises above the sediment surface.
- 8) Remove the upper stopper and siphon off water in the core tube without disturbing sediment collected. DO NOT pour water out of tube. This could cause loss of the fine grain portion of the sediment sample.
- 9) Remove the stopper from the top tube opening to release suction and the sediment core will come out or tap the tube on the pan that will be used to homogenize sample to release sediment. Note: If the sediment is packed tightly, a Teflon coated rod may be used to remove the sediment.
- 10) Take the top three centimeters of the sediment core sample and place it in the pan. Continue collection until sufficient sediment has been collected.
- 11) The subsamples should be homogenized in the pan by stirring with a spoon or scoop before removing an aliquot for placement in the container.
- 12) Continue collections until the required amount of sediment is obtained.
- 13) Place an aliquot of sediment in a glass jar, label it and place it in wet ice.
- 14) Every effort should be expended so that little or no standing water remains in the sample jar when shipped for analysis.
- 15) Scrub out any remaining sediment and rinse thoroughly with ambient water prior to sampling additional sites.

f.4.4) Boat and Bridge sampling

The two main types of dredges are Eckman and Ponar (or Petit Ponar).

The Eckman is designed for softer substrates of sand, silt or mud. The Eckman dredge is not suitable for hard or rocky substrates and is too light to use in fast currents.

The Ponar has been adapted with a top screen and side plates to prevent sample loss upon ascent. The Ponar may also be used in softer substrates, however it is the dredge of choice for rocky substrates.

f 4.4.1) Protocol

- 1) Open the jaws of the Eckman or Ponar dredge (depending on sediment type) and latch it so the dredge remains open.
- 2) Secure the spool end of the rope, which is attached to dredge, to the boat or bridge. Check the knot attaching the rope to the dredge to make sure it's secure.
- 3) Hold the dredge over edge of the boat or bridge and lower straight into water. DO NOT let the dredge “freefall”. It should be lowered and retrieved at about 1 foot per second.
- 4) Once the dredge hits the sediment, give the rope some slack and then pull up on the rope to force the dredge to close and take a bite of sediment from the streambed.
- 5) Pull the dredge out of the water and reopen jaws of the dredge to dump the sediment into a container (plastic or stainless steel dishpan). If the dredge did not collect any sediment, attempt the collection again. If the device is not collecting the sediment try moving the location slightly.
- 6) Use a Teflon spoon or an appropriate scoop to remove the top three centimeters of the dredged sediment and place it into the sample container. Care should be exercised to avoid touching or taking sample from near the edges of the sampling device.
- 7) Scrub out any remaining sediment and rinse thoroughly with ambient water prior to sampling additional sites.

f. 4.4.2) Criteria for accepting a sediment sample

- 1) The sample jar must not leak.
- 2) Desired penetration depth must be achieved. The dredge should penetrate enough to get the top 3 cm of sediment.
- 3) In the pan the sediment surface should be flat with no signs of disturbance or washout.
- 4) The sample surface should not be pressed against the top of the sampler or screen.
- 5) Overlying water should be minimized in the jar. If some water is present, decant it.
- 6) Anthropogenic material must not be present, such as plastics or other trash. Anthropogenic materials should be removed prior to placing the sample in the jar.

Section III: Field Quality Control Samples

A) Field Quality Control Samples for Water Matrix

A.1. General

There are specific requirements for entering QA/QC samples into the WQM module of CEDS2000. See Appendix D for details.

- 1) Analyte-free water (e.g. Deionized or Distilled water) is water in which all analytes of interest and all interferences are below method detection limits.
- 2) Analyte-free water shall always be used for blank preparation and for the final in-house decontamination rinse.
- 3) Analyte-free water shall be transported to the field in containers of suitable construction, such as cubitainers or large plastic jars.
- 4) Generally, equipment blanks and field duplicates are collected at the same station.

a) Equipment Blanks

- 1) The equipment blank tests for carry-over contamination between sampling sites. Equipment blanks are samples generated from the sampling equipment in use.
- 2) The equipment blank may be performed in the field between stations.
- 3) An equipment blank needs to be collected once for each 25 sites sampled (4%).
- 4) Flush or rinse sampler with analyte free water at least once prior to collecting the equipment blank.
- 5) Analyte free water is run through the sampling equipment (pump and hose, bucket etc.) and then poured into the respective sampling containers, preserved identically as samples normally collected and then sent to the lab to determine possible contaminants from sampling equipment.
- 6) If the equipment blank result is three times above the method detection limit, the data is suspect and will be removed from the database by the QA officer.

b) Field Duplicate Samples

- 1) Duplicate samples are two or more samples collected to determine sampling technique precision and/or laboratory precision. Sampling technique precision is determined by the collection of duplicate samples.

- 2) A field duplicate needs to be collected once for each 25 sites sampled (4%).
- 3) Using the appropriate sampling technique, obtain one bucket of water and fill two identical containers sequentially. If the pump and hose is used, attach a “Y” shaped adapter and fill the two identical containers at same time.
- 4) Duplicate samples will be collected, preserved and handled in accordance with the procedures with this manual.
- 5) The stations in which duplicate samples will be collected will be chosen randomly.

B) Quality Control Requirements for Sediments

a) Equipment Blanks

- 1) Equipment blanks test for carry over contamination between sampling sites. Equipment blanks are samples generated from the sampling equipment in use.
- 2) The equipment blank may be performed in the field between stations.
- 3) One equipment blank needs to be collected on each run where sediment sampling is being performed.
- 4) Analyte-free water is run through the sampling equipment and then poured into the respective sampling containers, preserved identically as samples normally being collected and then sent to lab to determine if there is possible contamination from the sampling equipment.
- 5) If the equipment blank results are three times above the method detection limits, the data is suspect and will be removed from the database by the QA officer.

b) Duplicate samples

- 1) Four percent of the sediment samples collected will be field duplicates.
- 2) The duplicate samples will be collected from one location as one sample of sufficient volume to homogenize and split it into two aliquots for analysis.
- 3) Duplicate samples will be collected and handled in accordance with procedures of this manual.
- 4) The station in which duplicate samples will be collected will be chosen randomly.

Section IV: Field Testing Procedures

Accument AP Series Handheld pH/mV/Ion Meter

SCOPE AND APPLICATION

This method is an electrometric procedure for measuring pH in surface and saline water samples.

PROCEDURE

1. General Procedures and Precautions

- (a) Rinse the electrodes thoroughly with distilled water after each sample or standard. Shake off excess water and blot dry.
- (b) Calibrate the meter each day before use with a minimum of two fresh standard buffer solutions that bracket the expected pH of the samples to be tested
- (c) If the sample pH reading is beyond the calibration standard value, recalibrate the meter with standards to bracket the sample pH. Previous measurements may need to be excluded.
- (d) After reading highly acidic or alkaline samples, rinse electrodes thoroughly with distilled water and check electrode response and calibration linearity. Allow additional time for equilibration.
- (e) Be sure to check the expiration dates on the pH buffers prior to using them for calibration/post-calibration.
- (f) The pH probe generally has a one-year shelf life.

2. Instrument Setup

- (a) For pH, mV, and Ion measurements, attach combination electrodes with BNC connectors directly to the middle BNC jack on the meter. If non-combination electrodes are used, adapters must be used.
- (b) If automatic temperature compensation is desired, insert the waterproof ATC connector into the ATC tower jack. Insert the attached plug if an ATC probe is not used to maintain a waterproof state.

- (c) The AC adapter jack lies next to the BNC jack opposite the tall ATC tower jack. Insert the attached plug to maintain the meter in a waterproof state. If an AC adapter is connected, the meter is not waterproof. When the AC adapter is in use, the battery is removed from the circuit, preventing battery drainage.
- (d) Press the on/off button to turn on the meter. Press setup twice and then enter to clear memory.
- (e) With the electrodes immersed in storage or buffer solution, press pH to enter the pH mode.

3. Instrument Calibration

- (a) For the first use of the day, press the setup key twice and then hit enter to clear the previous calibration data.
- (b) Press the mode key until the display indicates the instrument is in pH mode. Remove protective cap from electrode, rinse with distilled water and blot excess water with soft tissue.
- (c) Immerse electrode in the first buffer solution and stir briefly with electrode to remove bubbles from the electrode surface. If possible a magnetic stirrer should be used with all samples to insure homogenous mixing of solutions.
- (d) Depress the standard key and continue stirring. Be sure that the ATC probe is also immersed in the buffer solution. The standard 1 symbol and value should flash. When a stable reading is achieved, the auto symbol will stop flashing and the standard buffer value is displayed.
- (e) Press std to access the Standardize screen. The buffer group used by the meter will briefly be displayed, and the prompt press std to standardize will flash.
- (f) Press std again to initiate standardization. The meter will automatically recognize the buffer used, and display the value on the screen. Standardize will flash until the buffer is accepted, and the meter returns to the Measure screen. The accepted buffer value remains displayed on the screen.
- (g) Repeat steps 2-4 with a second and subsequent buffers. When the meter accepts the second buffer, it will briefly display the efficiency (as percent slope) associated with the electrode's performance prior to returning to the Measure mode. If the percent slope is outside the range of 90-102, the meter will display ELECTRODE ERROR and will not return to the Measure screen until you press enter. The message ELECTRODE ERROR will remain until an acceptable slope is attained after standardization.
- (h) Record all pH values onto the logsheet.

- (i) Place the plastic protective cap over the probe for transport. Make sure the cotton is saturated and placed in the bottom of the cap.

4. Field Measurement Procedures

- (a) If the instrument has been checked and calibrated, depress the on/off key to switch unit on.
- (b) Immerse the electrode into the sample solution. Stir moderately if possible. Note: Make sure the meter is in the pH mode.
- (c) When the meter senses that the reading is stable, STABLE will appear under the measurement reading. The reading may be recorded at this time.
- (d) If AUTO is not displayed on the screen, the autoread function is not active, and the meter will continuously monitor the pH value of the sample, and change as it changes.
- (e) If AUTO is displayed on the screen, the meter will fix the measured pH value on the screen when it is stable. AUTO will flash on the display until a stable reading is obtained.
- (f) Place the plastic protective cap on the probe making sure that the tissue is saturated.

5. QC limits

Check calibrations using standard buffer solutions at least once during or at the end of the sampling, and record the results in the calibration logsheet (see Appendix A) If the reading is off by more than ± 0.1 pH units, corrective action needs to be taken. The data collected during the day needs to be flagged.

6. Preventative Maintenance

6.1 Battery Requirements

- (a) The pH meter is powered by a 9-volt battery.

6.2 Replacing Batteries

- (a) The battery must be installed or replaced (1) prior to initial use, (2) when the main display area is blank, or (3) when the Low Battery (Lo?) indicator is on.

- (b) To install or replace the battery
- Remove the battery slipcover from the back of the meter.
 - Disconnect the old battery, and connect a new 9-volt battery.
 - Place the installed battery in meter battery compartment. Make certain that the battery wires are properly positioned so as not to interfere with the closing of the battery cover. Otherwise, the cover's edge may damage the wires.
 - Replace the battery slipcover.
- (c) If you desire to use line voltage, connect the AC adapter to the top connector AC power jack and to a power source. Note that the meter is not waterproof when the AC adapter is connected.

6.3 Instrument Electronics Check

- (a) Check the instrument for proper operation at least once a month using the following procedures. The results should be recorded in the logbook.
- (b) Disconnect the electrode cable from the meter. Press I, turn on the meter, then press C to clear. The display should show C and Auto symbol. If not, replace the batteries.
- (c) Insert one end of a paper clip into the small hole in the center of the 'pH' input connector.
- (d) Press 'pH' then 'STD'. The display should lock at pH 7.00, indicating a one-point standardization. If the meter fails, call the manufacturer for service.
- (e) Reconnect the pH electrode cable to the "pH" input connector. Insert one end of a paper clip into the small hole in the center of the electrode connector. Hold the other end of the clip to the inside barrel of the same connector.
- (f) Press 'pH' then 'STD'. The display should lock at pH 7.00. Press 'pH' then remove the paper clip. The reading should drift. If the meter fails, call the manufacturer for service.
- (g) Reconnect the pH electrode. Immerse the electrode in the pH 4 buffer and perform a one-point standardization. Then immerse the electrode in the pH 10 buffer and take a pH reading. At 25°C, the reading should be between 9.7 and 10.1 pH. If the test fails, the pH electrode is faulty and must be rejuvenated or replaced.

6.4 pH Electrode Rejuvenation

- (a) This meter can be directly fitted with combination electrodes only. If separate pH or ION and reference electrodes are employed, adapters are required. The meter also provides a jack for an ATC probe.

- (b) Carefully remove the protective cover from the end of the pH electrode. Before using the electrode, or if the electrode is dry, soak it for 2-4 hours in electrode storage solution, pH 4 buffer, or KCl solution.
- (c) Prepare and condition the ion selective electrode as recommended by the manufacturer.
- (d) Remove the shorting cap from the BNC connector. Install the electrode by twisting it to lock it in place.
- (e) Rinse and blot dry (don't wipe) the electrode between each measurement. Use distilled or analyte free water, or a portion of the next solution to be measured.
- (f) Between measurements, store the pH electrode in electrode storage solution, pH 4 buffer, or KCl solution. If liquid filled, always leave the filling hole open whenever the electrode is immersed in any solution. Refill when the level of fill solution recedes below the manufacturers recommended level.
- (g) Store your ion selective electrode as recommended by the manufacturer.

7. Spare Parts and Supplies

- (a) Buffer solutions pH 4, 7 & 10
- (b) Kim wipes or soft cloth
- (c) 9- Volt batteries
- (d) Automatic Temperature Adapter (ATC)
- (e) Combination liquid-filled pH/ATC electrode
- (f) AC adapter
- (g) Adapter (US Standard/Pin to BNC)
- (h) Adapter (dual pins to BNC)
- (i) Adapter (BNC/pin to single BNC)

Reference:

Accumet AP Series Handheld pH/mV/Ion Meter Instruction Manual, Fisher Scientific, 1998.

YSI Model 58 Dissolved Oxygen and Temperature Meter

A) Instrument Check

- 1) Before using the instrument, check the membrane selection switch to ensure it corresponds to the membrane used on the probe.

- 2) Check the probe for:
 - a) Condition of the membrane (wrinkled, dried out, air bubble)
 - b) Condition of the gold cathode (tarnished or silver plating)
 - c) Condition of the silver anode (discoloration)
- 3) Check the probe connection for security and tightness
- 4) Turn the instrument function switch to the zero position and allow the meter to stabilize for at least 15 minutes.

B) Daily Calibration

Calibrate the meter daily when in use. Calibration can be disturbed by physical shock, touching the membrane, fouling of the membrane or the drying out of the electrolyte solution.

Air calibration is normally easiest since the instrument compensates for temperature variation in that mode. However, the operator may elect to calibrate in the mg/l mode if he intends to take measurements in that mode, since doing so will eliminate any possible mode to mode error.

a) Air Calibration (% Saturation)

Air calibration is the quickest and by far the simplest calibration technique.

- 1) Turn the instrument function switch to the % saturation setting.
- 2) Place a moist sponge or a piece of cloth in the plastic calibration bottle. Loosen the bottle lid about ½ turn and slip the bottle over the probe guard up to the bottle. Place the probe in a protected location at room temperature.
- 3) Set the function switch to ZERO and readjust the display to read 0.00. Switch back to % air saturation mode.
- 4) After the display reading stabilizes unlock the O₂ calibration control knob locking ring.
- 5) Adjust the display to the calibration value indicated in the pressure/altitude chart printed on the back of the meter.
- 6) Re-lock the locking ring of the O₂ calibration control knob to prevent accidental changes in the calibration setting.
- 7) Record the % saturated DO into the logsheet.

b) Air Saturated Water Calibration

Alternatively calibrate the meter probe to mg/l measurements using the following procedures.

- 1) Air saturate a volume of water by aerating for at least 15 minutes at a constant temperature.
- 2) Place the probe in the sample and stir. Switch the function switch to TEMP.
- 3) From the oxygen solubility chart printed on the back of the meter determine and record the mg/l value corresponding to the temperature indicated.
- 4) Determine the local altitude or the true atmospheric pressure. Using the pressure/altitude chart on the back of the meter, determine the correct calibration value.
- 5) Multiply the mg/l value from the oxygen solubility table by the calibration value from the pressure/altitude table and divide by 100 to determine the correct mg/l oxygen content of the saturated sample.
- 6) Readjust to zero if necessary.
- 7) Check that the salinity knob is set at 0.
- 8) Turn the function switch to 0.1 or 0.001 mg/l setting.
- 9) Unlock the O₂ calibration control knob locking ring.
- 10) Adjust the display to the value calculated previously.
- 11) Allow two minutes to verify stability of the readings.
- 12) Readjust as necessary.
- 13) Relock the locking ring of the O₂ calibration control knob to prevent accidental changes to the calibration settings.

C) Field Measurement Procedures

D.O. Measurement Procedures

- 1) With the instrument prepared for use and the probe calibrated, place the probe in the sample. If the stirrer is to be used, connect it and turn the stirrer switch to ON.

- 2) Adjust the salinity control to the salinity of the sample.
- 3) Turn the meter function switch to ZERO and zero the meter with the O₂ ZERO knob if necessary.
- 4) Turn the meter function switch to the desired readout setting and read the D.O. value in mg/l when the meter reading has stabilized.

D) Maintenance

a) Field Probe Maintenance

- 1) Membrane life depends on usage. The average useful life is 2-4 weeks. However, membrane replacement may be required whenever large bubbles form in the electrolyte solution or if the membrane becomes fouled or damaged. Membrane replacement may be required if erratic readings are observed or the calibration is not stable.
- 2) Electrolyte solution can be prepared by making a saturated solution of reagent grade KCL and distilled water, and then diluting the solution 1:1 with distilled water. Adding two drops of Kodak photoflow per 100 ml of solution assures good wetting of the sensor but is not absolutely essential.
- 3) The gold cathode should always be bright and untarnished. Inspect the gold cathode whenever the membrane is changed. If tarnished, clean by wiping with a clean lint-free cloth, pencil eraser or hard paper. Rinse the sensor several times with the electrolyte solution, refill and install a new membrane.
- 4) Some gases can contaminate the sensor. This is evidenced by discoloration of the gold cathode. If the tarnish can not be removed by conventional methods, return the probe to the factory for service.

b) Probe Performance Checks

Every month when the probe is in daily use or whenever the probe response is slow or calibration is unstable, check the probe performance.

1) Speed of response

- ◆ Prepare and calibrate the probe.
- ◆ With the probe in air, switch to the % air saturation mode.
- ◆ Immerse the probe in a 25 °C O₂-depleted sample (2 g/l Sodium Sulfide)
- ◆ A proper functioning probe will down scale to 10% air saturation in 20 seconds or less.

2) Background Current

After performing the speed of response steps, leave the probe in the depleted sample for approximately five minutes. The reading should fall below 1-% air saturation.

3) Calibration Stability

- ◆ Carefully calibrate the probe in moist air inside the calibration bottle with the instrument set in the % air saturation mode.
- ◆ Allow the instrument to operate for one hour and recheck the calibration.
- ◆ A properly functioning probe will hold calibration within $\pm 1\%$ for one hour after the first hour of operation.

c) Probe Service

If any of the following conditions arise, the probe should be serviced accordingly:

- 1) Damaged or wrinkled membrane. Change the membrane and reset.
- 2) Fouled or silver coated gold cathode. Change the cathode.
- 3) Fouled silver anode. Soak for 24 hours in 3% ammonia, rinse thoroughly with distilled water and retest.
- 4) Damaged cable or connector. Inspect and replace if needed.

If these steps do not restore the probe's performance to specifications, return the probe to the
Factory service.

a) Meter Maintenance

When the Lobat warning shows on the display there are 50 hours of use remaining. This warning reminds the operator to change the batteries at their earliest convenience.

The instrument uses 4D sized carbon-zinc batteries. These batteries are located in the upper holder of the instrument. Remove the batteries if the instrument will be unused for long periods of time.

E) Quality Control

E.1) DO meter Calibration Checks

1) Daily

- a) Calibrate the meter in accordance with the procedures of this manual.
- b) Check the calibration at least once during sampling and at the conclusion of the day's sampling. Record the data onto the logsheet. If a calibration check is off $\pm 5\%$ of the calibration value, a corrective action needs to be taken. The data collected during that day needs to be flagged.

2) Monthly

- a) Fill a clean bucket with uncontaminated or analyte free water and place the probe into the bucket. Rinse the BOD bottle 1 or 2 times with the water from the bucket, discarding the rinse. Enter BOD bottle horizontally, avoid introducing air bubble into BOD bottle. Determine the DO by the Winkler method (see the method procedure in section V)
- b) If the air calibration seems to operate properly but the oxygen concentration disagrees with the average results of the Winkler value by more than 0.5 mg/l, it is time to have the electrode or meter serviced or replaced.

E.2) Temperature Calibration Check

All thermometric devices shall, at a minimum, be checked semi-annually in the laboratory against a National Institute of Standard and Technology (NIST) precision thermometer. Calibration is performed by partially immersing the thermometer and a NIST precision thermometer in a 1-liter glass beaker filled with crushed ice and water. The thermometers are allowed to equilibrate in the ice and water mixture for 10 minutes prior to recording temperature. Repeat the calibration with a water sample stabilized at about room temperature near 25 °C. Temperatures should agree within $\pm 0.5^{\circ}\text{C}$. Make note of the calibration in the logbook. If the thermoprobe does not meet the acceptance criteria, the thermoprobe needs to be serviced or replaced.

YSI Model 85 Handheld Oxygen, Conductivity, Salinity, and Temperature System

A) Preparing the Probe

The YSI Model 85 dissolved oxygen probe is shipped dry. The protective membrane cap on the probe tip must be removed and replaced with KCl solution and a new membrane cap before using the probe. Follow the instructions below to install KCl solution and the new membrane cap.

a) Membrane installation

- 1) Unscrew and remove the probe sensor guard.
- 2) Unscrew and remove the old membrane cap.
- 3) Thoroughly rinse sensor tip with analyte-free water.
- 4) Prepare the electrolyte solution according to the directions on the KCl solution bottle.
- 5) Hold the membrane cap and fill it at least $\frac{1}{2}$ full with the electrolyte solution.
- 6) Screw the membrane cap onto the probe until it is moderately tight. A small amount of electrolyte solution should overflow.
- 7) Screw the probe sensor guard on until it is moderately tight.

B) Calibration

a) Calibration of Dissolved Oxygen

- 1) Ensure that the sponge inside the instrument's calibration chamber is wet. Insert the probe into the calibration chamber.
- 2) Turn the instrument on by pressing the ON/OFF button on the front of the instrument. Press the MODE button until dissolved oxygen is displayed in mg/l or %. Wait for the dissolved oxygen and temperature readings to stabilize (usually 15 minutes is required).
- 3) Use two fingers to press and release both the UP ARROW and DOWN ARROW buttons at the same time.
- 4) The LCD will prompt you to enter the local altitude in hundreds of feet. Use the arrow keys to increase or decrease the altitude. When the proper altitude appears on the LCD, press the ENTER button once.
- 5) The instrument should now display CAL in the lower left of the display. The calibration value should be displayed in the lower right of the display and the current % reading should be on the main display. Make sure that current % reading is stable, then press the ENTER button. The display should read SAVE then should return to the normal operation mode.
- 6) Record the % saturated DO onto the logsheet.

b) Calibration of Conductivity

- 1) Turn the instrument on and allow it to complete its self-test procedure.
- 2) Select a calibration solution, which is most similar to the sample you will measure.

- 3) Place at least 3 inches of solution in a clean glass beaker.
- 4) Use the Mode button to advance the instrument to display conductivity.
- 5) Insert the probe into a beaker deep enough to completely cover the oval shaped hole on the side of the probe. Do not rest the probe on the bottom of the container. Suspend it above the bottom by at least $\frac{1}{4}$ inch.
- 6) Allow at least 60 seconds for the temperature reading to become stable.
- 7) Move the probe vigorously from side to side to dislodge any air bubbles from the electrodes.
- 8) Press and release the UP ARROW and DOWN ARROW buttons at the same time.
- 9) Use the UP ARROW and DOWN ARROW button to adjust the reading on the display until it matches the value of the calibration solution you are using.
- 10) Once the display reads the exact value of the calibration solution being used, press the ENTER button once. The word "SAVE" will flash across the display for a second indicating that calibration has been accepted.
- 11) Record the calibration value into the logsheet.

C) Taking Measurements

Once the batteries are installed correctly, press the ON/OFF button. The instrument will activate all segments of the display for a few seconds, which will be followed by a self-test procedure that will last for several more seconds. During the power on self-test sequence, the instrument's microprocessor is verifying that the instrument is working properly. The instrument will display the cell constant of the conductivity probe when the self-test is completed. If the instrument detects an internal problem, the display shows a continuous error message.

The Model 85 is designed to provide six measurements: Dissolved Oxygen %, Dissolved Oxygen mg/l, Conductivity, Specific Conductance, Temperature and Salinity. To choose one of the measurement modes above (temperature is always displayed) simply press and release the MODE button.

It is important to remember that the dissolved oxygen probe's accuracy is stirring dependent. This is due to the consumption of oxygen at the sensor tip during measurement. When taking dissolved oxygen measurements the probe must be moved through the sample at the rate of 1 foot per second to provide adequate stirring.

D) Quality Control

D.1) DO and Conductivity meter Calibration Checks

a) Daily

- 1) Calibrate the meter in accordance with the procedures of this manual.
- 2) Check the calibration at least once during sampling and at the conclusion of the day's sampling. Record the data onto the logsheet. If calibration check is off $\pm 5\%$ of the calibration value, corrective action needs to be taken. The data collected during that day needs to be flagged.

b) Monthly

- 1) Fill a clean bucket with uncontaminated or analyte free water and place the probe into the bucket. Rinse the BOD bottle 1 or 2 times with the water from the bucket, discarding the rinse. Submerge the BOD bottle horizontally to avoid introducing air bubbles into the BOD bottle. Determine the DO by the Winkler method (see method procedure in section V)
- 2) If the air calibration seems to operate properly but the oxygen concentration disagrees with the average results of the Winkler value by more than 0.5 mg/l, it is time to have the electrode or meter serviced or replaced.

D.2) Temperature Calibration Check

All thermometric devices shall, at a minimum, be checked semi-annually in the laboratory against a National Institute of Standard and Technology (NIST) precision thermometer. Calibration is performed by partially immersing the thermometer and a NIST precision thermometer in a 1-liter glass beaker filled with crushed ice and water. The thermometers are allowed to equilibrate in the ice and water mixture for 10 minutes prior to recording temperature. Repeat the calibration with a water sample stabilized at about room temperature (near 25 °C). Temperatures should agree within $\pm 0.5^{\circ}\text{C}$. Make note of the calibration in the logbook. If the thermoprobe does not meet the acceptance criteria, the thermoprobe needs to be serviced or replaced.

Hydrolab H2O Water Quality Multiprobe with Display

Field measurements of pH, Dissolved Oxygen, Conductivity, Temperature and Depth.

A) System Components

The four basic components of the Hydrolab water quality multiprobe are the probe, the display unit, the sample circulator and the battery pack.

- a. The multiprobe, in its sealed high pressure housing, contains all of the sensors for temperature, dissolved oxygen, conductivity, pH, and depth as well as the electronic circuits that sensors require for their operation. The sensors, in combination with the electronic circuits, provide the data signals that represent the values of the measured parameters.
- b. The display unit which operates at the opposite end of the data cable from the multiprobe. Depending upon the setting of its function key, the display unit sends signals down the cable directing the multiprobe to make a measurement of the selected parameter.
- c. The sample circulator is an electrically powered magnetic stirrer similar to laboratory magnetic stirrers. It is encased in a high-pressure weighted housing, which permits underwater operation.
- d. The auxiliary battery pack supplies power from a 12 volts recharger for the entire system.

B) Calibration of Parameters

General Procedures

Note: DO NOT turn off the display unit at any time during the calibration procedure. The newly calibrated data will not be saved if the unit is turned off.

Note: Maintain a calibration log sheet in which is entered all data pertaining to each precalibration, postcalibration, or maintenance procedure.

Calibration and postcalibration procedures should be performed on each day of use. The calibration sequence should follow the parameter order discussed below.

- 1) Replace storage cup on multiprobe with bottomless calibration cup. Take special care not to bump probes with hand or cup as this may result to damage to the probes.
- 2) After the calibration of each parameter, record the calibrated parameter value in the calibration sheet (in Appendix A) and be sure to store the data utilizing the display unit.
- 3) When the multiprobe battery reading drops below 10.0 volts, the scout 2 internal batteries should be replaced or external battery recharged as soon as possible after the low battery warning symbol appears for optimum system performance.
- 4) Check the expiration dates on all pH standards.

- 5) Specific Conductance standards should be fresh to within 6 months of the date of preparation.

C) Dissolved Oxygen

Note: It is good practice to get analyte-free water for calibration from carboy. The analyte-free water is stabilized to room temperature so the temperature equilibrium time will be reduced.

- 1) Check the membrane on the probe tip to see if it is wrinkled, bubbled, torn, dirty, or otherwise damaged. If so, service the probe in accordance with the manufacturer's operation manual. It is, however, good practice to replace the membrane on a regular schedule, before trouble becomes visible. Frequent changes of the electrolyte solution will maximize the life of the sensor.
- 2) With the multiprobe oriented so that the sensors are pointed toward the ceiling, fill the calibration cup with analyte-free water until the water is just level with the o-ring used to secure the membrane.
- 3) Carefully remove any water droplets from the membrane with the corner of a tissue (DO NOT apply pressure to surface) and cover the open top of the calibration cup to prevent air currents from affecting calibration.
- 4) Determine the laboratory barometric pressure in mm Hg from a barometer and record the data in the appropriate spaces on the data sheet.
- 5) Turn on the Scout 2 unit with the on/off button. Wait for 5 minutes to allow air in the cup to become water saturated. The sensor is ready for calibration once the readings have stabilized. Record the initial meter dissolved oxygen reading on the meter calibration log sheet.
- 6) Determine the temperature from the sonde and record the data in the appropriate space on the data sheet. Read the Oxygen concentration from the table based on temp. in Celsius degrees as determined by the far left column and first row of the chart. Multiply the Oxygen concentration by the correction factor as determined by the barometric pressure (mmHg). Press calibrate and use right arrow key to choose (%). Press in the barometric pressure in mmHg from a barometer or the calculated value. Press enter; Use left arrow key to choose (yes) to save the calibration. The unit will send a DO value (mg/l) to display. Press screen and note that %Sat equals 100.0 for correct DO calibration. Read the value of DO mg/l from screen and record in the appropriate space on the logbook. Compare the value of table DO and Sonde DO. They must compare within $\pm 0.5\text{mg/l}$.

Note: The conversion factor from inHg to mmHg is 25.4.

D) Specific Conductance

Note: Readings are most accurate when they lie within the calibrated range. Determine the expected range of values in the field prior to calibration.

- 1) Rinse the sensors twice with a small portion of the specific conductance standard to be used for calibration, discarding the rinse each time.
- 2) With the calibration cup screwed onto the multiprobe, sensors pointed toward the ceiling. Fill calibration cup with **fresh** standard solution to about one centimeter below the top. Be sure no bubbles are trapped in the bores of the cellblock.
- 3) Watch the specific conductance readings until they have stabilized; the sensor is now ready for calibration. Record the initial meter specific conductance reading on the meter calibration log sheet.
- 4) Press calibration and use the left arrow key to choose c press enter. Use up, down, and right arrows to enter the value of your specific conductance standard. Press enter. Use the left arrow key to choose Y (yes) to save the calibration. The unit will send the standard value to display. Record the standard value in the logbook.
- 5) Pour standard solution into a storage bottle for use as the standard rinse in the next calibration. Discard after using for the rinse.

Note: The following table shows several potassium chloride solutions and their specific conductance values.

KCL Molar Concentration	Specific Conductance in (ms/cm)
0.5M	58.64
0.1M	12.90
0.05M	6.668
0.01M	1.413
0.005M	0.718
0.001M	0.147

E) pH

Note: Calibrate the instrument with pH buffer that brackets the range of values anticipated in the field.

- 1) Flush the calibration cup and sensors thoroughly 3 times with analyte-free water.

- 2) Rinse twice with a small amount of pH 7.0 buffer saved from previous calibrations to saturate the sensors. Discard the buffer after each rinse.
- 3) Fill cup with **Fresh** pH 7.0 buffer sufficient to cover the sensor.
- 4) Allow two minutes for thermal equilibrium. Record the pH value displayed in the logbook.
- 5) Press calibrate and enter choose (P). use the up, down, and right arrows to enter the pH of the zero standard (7.00), presses enter. Use the left arrow to choose Y (yes) to save calibration. The unit will send a pH value to the display. Record the pH value in the logbook.
- 6) Pour buffer into a storage bottle for use as the rinse in step 2 of the calibration.
- 7) Flush the calibration cup and sensors thoroughly twice with analyte-free water.
- 8) Rinse the cup and sensors twice with a small amount of pH 10.00 or pH 4.00 buffer.
- 9) Fill the calibration cup with **FRESH** pH 10.00 or pH 4.00 buffer to cover the sensor and wait for the instrument to equilibrate.
- 10) Record the pH value displayed in the logbook.
- 11) Press calibrate and enter to choose (P). Use up, down and right arrows to enter the pH of the slope standard, presses enter. Use the left arrow to choose Y (yes) to save calibration. The unit will send a pH value to the display. Record the value in the logbook.
- 12) Pour the buffer into a storage bottle. Flush the calibration cup and sensors thoroughly three times with analyte-free water.
- 13) Replace the storage cup.
Place a sufficient amount of tap water in the storage cup to keep the DO membrane moist. Do not allow the water to come in contact with the sensors as an ionic gradient may develop resulting in dilution of the electrolyte solutions.

E.2) Temperature Calibration Check

Central office personnel will conduct temperature checks for multiprobes against an NIST certified thermistor annually when conducting site visits.

Regions should check the temperature probe against another multiprobe instrument's temperature probe semi-annually. If a discrepancy should occur (temperatures are not ± 1 °C) contact Central office so that the probes can be checked against an NIST certified thermistor as soon as possible. If there is good agreement between the instruments, then Central office personnel will check the instruments against an NIST certified thermistor as planned.

The temperature check should be conducted in an ice/water mixture (e.g. 4 °C) and at a warm water temperature that will best approximate the highest ambient temperature expected to be sampled (e.g. 25-30 °C) where the probe(s) and/or NIST certified thermistor are lowered into the mixtures simultaneously and read.

Send the Hydrolab unit back to the manufacturer for temperature calibration if the thermistor and Hydrolab values differ more than 0.5 °C.

F) Depth

Depth can be calibrated to zero in the air, at or near the surface of the water to be sampled.

G) Hydrolab field set-up and operation

The basic Hydrolab consists of: the display unit, the data cable, the sonde, the sample circulator, and the battery pack. If additional weight is needed, a lead weight can be attached to the nylon line.

H) Preparation for use

- 1) Interconnect the display unit, battery pack, and data cable. Carefully place the instrument back in its case. Coil the cable and keep it kink-free.
- 2) Remove the storage cup from the Sonde and screw on the circulator in its place. Connect the two ends of the data cable to the probe and circulator. Ensure that the probe is attached to the data cable with the pin and clip ring.
- 3) Fill the sonde storage bucket with sample water so that the sensors will be submerged. Store the sonde in a bucket of water when not in use. Alternately, remove circulator (do not disconnect) and replace storage cup filled half full with sample water.
- 4) Ensure that the magnetically coupled impeller on the stirrer base is properly lubricated and rotating free on its shaft. Any obstruction to smooth rotation of the impeller may cause erratic DO measurements and excessive power drains to the battery.

5) Turn the display unit switch to OFF.

I) Field Set-up and Operation

- Hydrolabs must be precalibrated and the operation checks must be Performed prior to using it in the field.
 - While the unit is in operation aboard the vessel, the boat operator must maintain the boat's position and orientation with wind and tide movement to ensure that the Sonde hangs as vertically as possible.
 - While the unit is in the operation aboard the vessel, keep the probe away from the engine's propeller to ensure the safety of the Sonde and data cable, and to prevent interference from the propeller wash with all water quality measurements.
- 1) Remove the unit from storage.
 - 2) Screw on the circulator. – Remove the storage cup from the Sonde and screw on the circulator in its place. Caution should be taken to avoid any contact with the sensors.
 - 3) Connect the two ends of the data cable to the probe and circulator. – Ensure that the probe is attached to the data cable with the pin and clip ring.
 - 4) Calibrate depth. – At the station above the surface water, press the depth key.
 - 5) Fill the Sonde storage bucket with sample water. – When not in use, store the Sonde in a bucket of sample water. Fill the bucket such that the entire Sonde unit will be submerged.
 - 6) Visually inspect the magnetic impeller on the stirrer base. – Make sure magnetic impeller is rotating freely on its shaft. Any obstruction to smooth rotation of the impeller may cause erratic DO measurements and excessive power drains to the battery.
 - 7) Lower the Sonde to 0.3 meter below the surface. Turn the unit on.
 - 8) Wait for thermal equilibrium. – Allow thermal equilibrium and then verify that the dissolved oxygen reading is stable. The D.O. sensor is the slowest of all the Sonde sensors to equilibrate, therefore, wait for this reading to stabilize before recording it on the field sheet.
 - 9) Turn the display unit off and retrieve the Sonde - At the end of the day put the storage cup back on the Sonde and place the unit in its storage bag in the vehicle. This will allow the Sonde to equilibrate quicker for postcalibration of the parameters.

J) Hydrolab Postcalibration

Note: DO NOT CALIBRATE THE INSTRUMENT TO THE STANDARD VALUES DURING POSTCALIBRATION CHECKS. Perform postcalibration before cleaning up and servicing the sensor. When performing the postcalibration of the system, it is extremely important that the room temperature, sonde temperature, analyte-free temperature, and all standard solutions are at thermal equilibrium. If thermal equilibrium needs a long time or postcalibration values are outside the QC criteria, postcalibrate on next day is recommended.

a) Dissolved Oxygen

- 1) Follow the procedures described in section D
- 2) Record the data on the logbook. Compare the Saturated DO values from the chart and the instrument values as recorded in the logbook. If the difference between the two is less than 0.5 mg/L the instrument is in calibration. If the difference between the Saturated DO value and the instrument indicates that the instrument is not in calibration, check again the next morning to make sure that the temperature was properly equilibrated. If the difference is still greater than or equal to 0.5 mg/L the data collected during the sampling event is suspect and will be removed from the database by the QA officer. Additionally, the instrument should not be utilized until more extensive cleaning/maintenance is conducted and the instrument calibrates well.

b) Specific Conductance

- 1) Follow the procedures described in section D

Record the data on the logbook. Compare the displayed value to the saturated oxygen value. If the difference is ≤ 0.5 ms/cm for the 12.89 standard, ≤ 1.0 ms/cm for the 58.6 standard, ≤ 0.017 ms/cm for 1.413 standard or ≤ 0.02 ms/cm for the 0.147 standard the instrument is in calibration. If the instrument is not in calibration, check again the next morning to make sure that the temperature was properly equilibrated. If the difference is still ≥ 0.5 ms/cm for 12.89 standard, ≥ 1.0 ms/cm for the 58.6 standard, ≥ 0.017 ms/cm for 1.413 standard, or ≥ 0.02 ms/cm for the 0.147 standard the data is suspect and will be removed from the database by the QA officer. Additionally, the Hydrolab should not be utilized for that parameter until it has an extensive cleaning/maintenance.

c) pH

- 1) Follow the procedures described in section D

Record the data in the logbook. Compare the displayed values to the standard values. If the difference between the standard utilized and the value displayed is ≤ 0.2 units the pH is in calibration. If the difference indicates that the instrument is not in calibration, check again the next morning to make sure that the temperature was properly equilibrated. If the difference is still ≥ 0.2 units the data is suspect and will be deleted from the database by the QA officer. Additionally, the Hydrolab should not be utilized for that parameter until it has an extensive cleaning/maintenance.

K) Preparation of KCL Standards

Note: If the KCL 1 Molar stock solution is purchased from a supplier, be sure to the stock solution is not out of date prior to using it. If a powder is utilized to make the 1 Molar KCL stock solution, be sure not to use the solution after six months of preparation.

Prepare the KCL solution to be used in calibration after determining the desired conductivity range. Dilute prepared 1 Molar KCL stock solution to desired molarity using appropriate volumetric glassware.

K.1) Preparation of 1 Molar KCL stock solution:

- 1) Weigh out carefully 74.557 grams of reagent grade KCL salt on the balance.
- 2) Transfer the salt to a 1000 ml volumetric flask and fill to the mark with analyte-free water.
- 3) Gently agitate solution until KCL is completely dissolved.
- 4) Label a 1000 ml rectangular storage bottle while waiting for salt to dissolve. Write " 1M KCL Stock Solution", Your initial, and date prepared.
- 5) Transfer the prepared solution to a storage container.

K.2) Preparation of Working Standards:

- 1) 0.1 Molar KCL Standard Solution

- a) Measure out 100 ml of 1 Molar stock solution using a class A 100 ml volumetric flask.
 - b) Transfer the stock solution to a 1000 ml volumetric flask. Rinse 100 ml flask twice with analyte-free water pouring the rinse into the 1000 ml flask.
 - c) Fill 1000 ml flask to the mark with analyte-free water.
 - d) Gently agitate and transfer to the 1000 ml rectangular storage bottle.
 - e) Label the container with “ 0.1M KCL Solution”, your initials, and the date of preparation.
- 2) 0.05 Molar KCL Standard Solution
 - a) Follow the procedures for making the 0.1 molar KCL Standard Solution using 50 ml of 1 Molar stock solution and a class A 50 ml volumetric flask.
 - 3) 0.01 Molar KCL Standard Solution
 - b) Follow the procedures for making the 0.1 molar KCL Standard Solution using 10 ml of 1 Molar stock solution and a class A 10 ml volumetric flask.

L) Maintenance

L.1) Dissolved oxygen

DO sensor maintenance is usually required when calibration becomes impossible or when the membrane covering the cell becomes wrinkled, bubbled, torn, dirty or otherwise damaged. Follow a regular schedule for membrane replacement.

- 1) Remove the o-ring securing the membrane. Shake out the old electrolyte.
- 2) Rinse the sensor cavity with analyte-free water. Refill with fresh D.O. electrolyte solution (2M KCL) until a precipitable meniscus of electrolyte forms above the entire electrode surface of the sensor. To remove any bubbles trapped in the electrolyte solution, tap gently on the side of the D.O. sensor.

- 3) To replace the membrane, hold both ends of the membrane between the thumb and index finger of both hands. Hold the membrane above the top and carefully drop the membrane over the top of the sensor.
- 4) Place the new o-ring over the gold cathode. Do not use any type of grease on the o-ring. Secure the membrane with the o-ring by pushing down with your thumbs on both side of the o-ring. Carefully trim the excess membrane extending below the o-ring with the pair of scissors or the pocket of knife.
- 1) Allow the membrane to relax two hours minimum, 24 hours recommended before calibration.

L.2) Conductivity

To determine the appropriate maintenance, you need to carry out a periodic visual inspection of the sensor comparing your pre- and post-calibration results to the conductance standards used.

- 1) Remove the screws securing the conductivity cellblock. Pull the cellblock out.
- 2) Remove the five small o-rings that are slipped over the electrodes. Polish the entire exposed surface of the electrodes with emery cloth strips. Be careful not to scratch the nearby pH glass electrode.
- 3) Replace the five o-rings.
- 4) Clean the electrodes and the cellblock with the brush and some methanol or a methanol-soaked cotton swab.
- 5) Rinse the electrodes and the cellblock with analyte-free water.
- 6) Wet the five o-ring s with water to allow a better seal. Do not use any type of grease. Install the o-rings. Reinstall the conductivity cellblock. Insert and tighten the screws just enough to make sure that the cellblock is seated flat against the conductivity sensor body.
- 7) Rinse the sensor with analyte-free water twice. Let the sensor soak in tap water overnight to allow the freshly polished electrode surfaces to re-equilibrate with an aqueous environment.

L.3) pH Electrode

The pH electrode obviously requires maintenance when coated with oil, sediment, or biological growth. Slow response or non-reproducible measurements are signs that the electrode has become coated or scratched.

- 1) Wet a cotton ball, swab, or a clean soft non-scratching cloth with methanol. Carefully clean the pH glass electrode. This procedure will help remove any film on the glass and restore the speed of response.
- 2) Rinse the electrode with analyte-free water.

L.4) pH reference electrode maintenance

- 1) Unscrew the Teflon junction. Pour out the old electrolyte solution.
- 2) Use a hypodermic syringe to rinse the reference electrode housing with standard electrolyte solution (3M KCL saturated with silver chloride). Pour out the solution and then use the hypodermic syringe to fill the housing with standard electrolyte solution. Make sure that no bubbles are trapped in the reference electrode housing after it has been filled.
- 3) Use a standard screwdriver to screw the Teflon junction back on.

L.5) Temperature Sensor

Keeps the thermistor tube clean (free of barnacles or other deposits). Otherwise, the temperature sensor does not require any maintenance.

Hydrolab Data Sonde and Minisonde Multiprobe with Surveyor

A) Calibration of Parameters

a) General Procedures

- 1) Perform the calibration and post calibration procedures specified below on each day of use.
- 2) DO NOT turn off the display unit at any time during the calibration procedure. The newly calibrated data will not be saved if the unit is turned off.
- 3) Maintain a calibration log sheet in which all data pertaining to each precalibration, postcalibration, or maintenance procedures are entered.

- 4) Replace the storage cup on multiprobe with a bottomless calibration cup. Take special care not to bump the probes with your hand or the cup as this may result in damage to the probes.
- 5) After calibrating each parameter, record the calibrated parameter values in the calibration sheet (see Appendix A) and be sure to store the data utilizing the display unit.
- 6) When the surveyor internal battery reading drops below 7.2 volts, the surveyor internal batteries should be recharged.
- 7) Standards should be selected that best mimic the anticipated ambient sampling conditions.

Datasonde and Minisonde Pre-Calibration

a) Specific Conductance

Conductivity requires a two-point calibration. You need to calibrate your sensor to "0" first, then to the value of the slope standard you are using.

- 1) Dry conductivity probe opening with Q tip or soft cloth.
- 2) Select "setup/cal", "calibrate", "Sonde", "SpCond:us/cm", "Select". Select the number 0 using the arrow key and select "done". Press any key and select "go back". SpCond will read 0.0
- 3) Rinse with the conductivity standard you are using for the slope calibration. Discard the rinse solution.
- 4) Completely fill the calibration cup with fresh conductivity standard. The DO sensor must be covered. Allow the temperature equilibrate until conductivity reading are stable. Record the initial conductivity reading in the calibration log book.
- 5) If the circulator is not on, turn it on by selecting "setup/cal", "setup", "sonde". Using the arrow key to choose "circlor : Off/On", press "select". Select the number 1 using the arrow key and select "done".
- 6) Select "setup/cal", "calibrate", "sonde" then "SpCond: us/cm". Using the arrow key, enter in the value of the standard in use and press "done". Press any key and select "go back". SpCond will read the value of the standard. Record the calibration conductivity value in the logsheet.

b) pH

- 1) Rinse the sensors with analyte-free water vigorously for 6 seconds. Discard rinse water.
- 2) Rinse sensors using the "zero" buffer (value between 6.8 and 7.2). Discard the rinse solution and fill the cal cup with fresh buffer solution. The pH sensor must be covered. Allow readings to stabilize and record the initial reading in the calibration logbook.

- 3) Select “setup/cal”, “calibrate”, “sonde” then using down arrow key to find “pH:units” the “select”. Using the arrow key, enter the value of the standard being used and select “done”. Press any key and select “go back”. Allow the pH reading to stabilize. Record the calibration pH value in the logsheet.
- 4) Rinse the sensor with analyte-free water and discard.
- 5) Rinse with the pH buffer that will be used as a “slope” buffer (value either 4 or 10). Discard rinse solution. Fill the cal cup with fresh buffer solution, pH sensor must be covered. Allow the pH reading stabilize and record the initial reading in the calibration logbook.
- 6) Select “setup/cal”, “calibrate”, “sonde” then using down arrow key to find “pH:units” the “select”. Using arrow key, enter the value of the standard being used and select “done”. Press any key and select “go back”. The pH reading must remain stable. Record the calibration pH value in the logsheet.
- 7) Once the pH calibration is completed, turn the power off and the Hydrolab is ready to use.

c) Dissolved Oxygen

Note: It is good practice to get the water to be used for precalibration from a carboy. The water will have stabilized to room temperature so the temperature equilibrium time will be reduced.

- 1) If the circulator is on, Turn it off by selecting “setup/cal”, “setup”, “sonde”. Using the arrow key choose “circulator: Off/On”, press “select”. Select the number 0 using the arrow key and select “done”.
- 2) Fill the cap cup with water to just below the O-ring of the DO probe.
- 3) Using a kimwipe or other soft towel, carefully remove any water droplets from the DO membrane. Do not apply pressure to the membrane.
- 4) Cover the calibration cup loosely with the plastic storage lid, and allow the unit to equilibrate until the temperature reading is stable. Record the initial reading in the calibration log book.
- 5) Determine the temperature and Barometric pressure from the display unit and record the data in the appropriate spaces on the logsheet.
- 6) Select “Setup/Cal”, “Calibrate”, “Sonde”, “DO%: Sat” Then “Select”. Enter the value of the current barometric pressure in mmHG. Press any key and select “go back”.
- 7) Read the Oxygen concentration from the table based on temp. in Celsius degree as determined by the far left column and first row of the Saturated Dissolved Oxygen Chart (see Appendix B). Multiply the Oxygen concentration by the correction factor determined by barometric pressure (mmHg). The DO (mg/l) reading should be within ± 0.2 mg/l of the calculated saturated DO.
- 8) Record both DO values (mg/l) in the logsheet.
- 9) Replace the storage cup.
Place a sufficient amount of tap water in the storage cup to keep the DO membrane moist. Do not allow the water to come in contact with the sensors

as an ionic gradient may develop resulting in dilution of the electrolyte solutions.

d) Temperature Calibration Check

Central office personnel will conduct temperature checks for multiprobes against an NIST certified thermometer annually when conducting site visits.

The temperature function for the Hydrolab is set at the factory and can not be calibrated and corrected in the field. There is no field calibration procedure for temperature but rather a QC check to verify proper function. Regions should check the temperature probe against another multiprobe instrument's temperature probe semi-annually. If a discrepancy should occur (temperatures are not ± 1 °C) contact Central office so that the probes can be checked against an NIST certified thermometer soon as possible. If there is good agreement between the instruments, then Central office personnel will check the instruments against an NIST certified thermometer as planned.

The temperature check should be conducted in an ice/water mixture (e.g. 4 °C) and at a warm water temperature that will best approximate the highest ambient temperature expected to be sampled (e.g. 25-30 °C) where the probe(s) and/or NIST certified thermometer are lowered into the mixtures simultaneously and read. Send the Hydrolab unit back to the manufacturer for temperature calibration if the thermometer and Hydrolab values differ more than 1 °C

e) Barometric Pressure Sensor Calibration

To check if the Minisonde or Datasonde Barometric Pressure should be calibrated compare the instrument value to the barometric pressure in mmHg read from a barometer.

If a barometer is not available it can be estimated using the following formula:
 $BP \text{ (mmHg)} = 760 - 2.5(A_{ft}/100)$ where 'A_{ft}' is the local altitude above sea level in feet.

If the BP value in the Surveyor differs from either the barometer value or the estimated value, the sensor needs to be calibrated.

For calibration, a corrected barometric pressure should be obtained from a barometer (mm Hg) or from the local weather bureau (inches Hg). (convert the inches of Hg to mm Hg by multiplying it by 25.4) .Plug the corrected barometric pressure from the barometer or local weather bureau in mm Hg into the following formula to obtain the uncorrected BP that will be used in the calibration:

$$\text{uncorrected BP (mmHg)} = \text{corrected BP (mmHg)} - 2.5(A_{ft}/100)$$

To calibrate BP sensor :

- 1) disconnect the surveyor from the datasonde/minisonde.
- 2) Turn on the surveyor.
- 3) Select "setup/cal"
- 4) Select "calibration"
- 5) Select "BP Svr4: User cal" and press select
- 6) Using the arrow key, to enter the uncorrected BP in mmHg calculated above and press done

B) Preparation for use

- 1) If the short calibration cable is used for calibration, switch the calibration cable to a longer cable.
- 2) Remove the storage cup from the sonde, screw on the sensor guard and store the sonde in a moist environment when not in use.

C) Field operation, Postcalibration and Maintenance:

The Datasonde and Minisonde Field operation, postcalibration check procedures and maintenance are identical to those of the H20 model Hydrolab in section J.

Quanta

A) Calibration Preparation:

- 1) Select a calibration standard whose value is nearest those expected to be observed in the field.
- 2) Clean and prepare the sensors.
- 3) Attach the calibration cup.
- 4) Using the calibration cap, thoroughly rinse the sensors several times by half-filling the calibration cup with analyte-free water and shaking the transmitter to make sure each sensor is free from contaminants that might alter your calibration standard.
- 5) In a similar manner, rinse the sensors twice with a small portion of calibration standard prior to calibrating with the standard discarding the rinse each time.
- 6) Discard used calibration standards appropriately. **Do not attempt to reuse calibration standards.**

B) Calibration

a) Specific Conductance

- 1) Pour the specific conductance standard to within a centimeter of the top of the cup and make sure there are **no bubbles** in the measurement cell of the specific conductance sensor.
- 2) Selecting the Calib icon allows calibration of specific conductance. After selecting Calib, the Calib icon will remain lit in the operation icons and the

parameter digits and units icons will be blank. The heading icons will display the items that can be calibrated.

- 3) From the displayed heading icons, select the item to be calibrated. The selected one will blank. The parameter digits show the current value for the item selected. Press the arrow to change the numeric value to match the calibration standard. Once the value is correct, press the enter key to send the updated calibration value to the transmitter.
- b) Dissolved Oxygen % Saturation
- 1) Fill the calibration cup with deionized or tap water (specific conductance less than 0.5 ms/cm) until the water is just level with the o-ring used to secure the membrane.
 - 2) Carefully remove any water droplets from the membrane with the corner of a tissue.
 - 3) Turn the black calibration cup cover upside down (concave upward) and lay it over the top of the calibration cup.
 - 4) Determine the barometric pressure for entry as the calibration standard.
 - 5) Select the DO%/BP from Calib icon, enter barometric pressure and press the enter key.
- c) pH
- 1) pH is a two points calibration. A pH standard 7 is treated as the “zero” and all other values are treated as the “slope”. First calibrate “zero” then calibrate “slope”.
 - 2) Pour the pH 7 standard to within a centimeter of the top of the cup.
 - 3) Selecting “pH” from Calib icons. Press the arrow to change the numeric value to enter “7” and press enter key.
 - 4) Rinse the transmitter with analyte free water thoroughly.
 - 5) Pour the pH 4 or 10 standard to within a centimeter of the top of the cup.
 - 6) Press the arrow to change the numeric value to enter “4” or “10” and press enter key.
- C) Maintenance
- a) Specific Conductance
- 1) Clean the oval measurement cell on the specific conductance sensor with a small, non-abrasive brush or cotton swab.
 - 2) Soap or rubbing alcohol may be used to remove grease, oil or biological material.
 - 3) Rinse with water.
- b) Dissolved Oxygen
- 1) Remove the o-ring securing the DO membrane.
 - 2) Shake out the old electrolyte and rinse with fresh DO electrolyte.
 - 3) Refill with fresh DO electrolyte until there is a perceptible meniscus of electrolyte rising above the entire electrode surface of the sensor.

- 4) Make sure there are no bubbles in the electrolyte.
- 5) Hold one end of a new membrane against the body of the DO sensor with your thumb and with a smooth, firm motion, stretch the other end of the membrane over the sensor surface and hold it in place with your index finger.
- 6) Secure the membrane with the o-ring.
- 7) Make sure there are no wrinkles in the membrane or bubbles in the electrolyte.
- 8) Trim away the excess membrane extending below the o-ring.
- 9) Let the sensor soak overnight to allow the membrane to relax to its final shape.

c) pH

- 1) If the sensor is obviously coated with oil, sediment or biological growth, clean the glass with a very clean, soft, non-scratching cloth wet with rubbing alcohol.
- 2) Rinse with tap water.

d) pH reference electrode

- 1) Gently pull the entire reference sleeve away from the transmitter. The reference sleeve is the clear blue tube with a porous Teflon Reference Junction attached.
- 2) Discard the old electrolyte from the reference sleeve.
- 3) Drop two KCL salt rings into the reference sleeve.
- 4) Refill the sleeve to the top with reference electrolyte.
- 5) With the transmitter sensors pointed toward the floor, push the full reference sleeve back on to its mount until sleeve has just covered the first o-ring located on the mount.
- 6) Turn the transmitter so that the sensors point toward the ceiling and push the sleeve the rest of the way onto its mount.
- 7) Rinse with tap water.

D) postcalibration check

The Quanta postcalibration check procedures and criteria are identical to those of the H20 model Hydrolab in section J.

YSI 6000UPG Multi-Parameter Water Quality Monitor

Field measurements of Dissolved Oxygen, Conductivity, Temperature and Depth.

A) System Components

The four basic components of the YSI water quality multi-probe are the probe, display unit, external battery pack and the patented Rapid Pulse Dissolved Oxygen sensor.

The multi-probe, in its sealed high pressure housing, contains sensors for temperature, dissolved oxygen, conductivity, and depth, as well as the electronic circuits required for sensor operation. The sensors, in combination with the electronic circuits, provide the data signals that represent the values of the measured parameters.

The display unit operates at the opposite end of the data cable from the multi-probe. Depending upon the setting of its function key, the display unit sends signals down the cable directing the multi-probe to make a measurement of the selected parameter.

A patented Rapid Pulse Dissolved Oxygen Sensor exhibits low stirring dependence and, therefore, provides accurate results without an expensive and bulky stirrer. Because no stirring is required, battery life is extended and sensor drift caused by passive fouling is minimized.

The multi-probe operates using eight C-size alkaline batteries. These batteries are easily replaced in the field without disassembly of the unit and may last up to 90 days during normal use.

B) Calibration of Parameters

General Procedures

Note: Maintain a calibration log book in which all data is entered pertaining to each precalibration, postcalibration, or maintenance procedure.

Place the calibration cup over the outside of the sonde probe guard. It is not necessary to remove the guard to calibrate the sensors

After the calibration of each parameter, record the calibrated parameter value in the calibration logbook and be sure to store the data utilizing the display unit.

C) Dissolved Oxygen

Note: It is good practice to get DI water from carboy. The DI water has been stabilized for the room temperature so that the temperature equilibrium time will be reduced.

Check membrane on probe tip for wrinkled, bubbled, torn, dirty, or otherwise damaged. If present, service probe in accordance with manufacturer's operation manual. It is, however, good practice to replace the membrane on a regular schedule, before trouble becomes visible. Frequent electrolyte change will maximize the life of the sensor.

Replace the sonde guard bottom plate. Place a wet sponge inside a clean, empty calibration cup. Place the probe end of the sonde into the calibration cup. The oxygen probe will now be in water-saturated air. Insure that the calibration cup being used is vented or pressure released.

Press Esc to return to the sonde Main menu. Select 1. Run from the sonde Main menu to view the Run menu. Select 1. Discrete sample from the Run menu to view the Run Discrete-sample menu. Select 3. Sample interval from the Run Discrete-sample menu. Set the interval to 4 seconds and press Enter. Select 1. Start discrete sample from the Run Discrete-sample menu.

After 4 seconds have passed, data will begin to display on the screen. Wait 10-15 minutes. During this time the air will become saturated with water vapor and the D.O. sensor will warm-up and stabilize. After 10-15 minutes use the Esc key to return to the sonde Main menu.

Select 2. Calibrate from the sonde Main menu to view the Calibrate menu. Select 2. DO % to access the DO% calibration procedure. Enter the current barometric pressure in mm Hg. Press Enter and the computer will indicate that the calibration procedure is in progress.

After approximately 1 minute, the calibration will be complete. Press any key, as instructed, and the screen will display the percent saturation value which corresponds to your local barometric pressure input. For example, if your barometer reads 742 mm Hg, the screen will display 97.6% (742/760) at this point.

After the calibration is complete, press any key to return to the Calibrate menu.

Note: The conversion factor from inHg to mmHg is 25.4.

D) Specific Conductance

Note: Readings are most accurate when they lie within the calibrated range. Determine expected range of values in the field prior to calibration.

Note: This procedure calibrates both conductivity and specific conductance.

Rinse the sensors with a small portion of the specific conductance standard to be used for calibration and discard the rinse. Gently dry off the sensor before proceeding.

Without removing the sonde guard, slowly and carefully immerse the probe end of the sonde in the solution. Gently rotate and /or move the sonde up and down to remove any bubbles from the conductivity cell. The probe must be immersed past its vent hole.

Allow at least 1 minute for temperature equilibration before proceeding. Select 1. Conductivity to access the Conductivity calibration procedure and then 1. Sp. Cond. to access the specific conductance calibration procedure. Enter the calibration value of the standard you are using (mS/cm at 25 C) and press Enter. The current values of all enabled sensors will appear on the screen and will change with time as they stabilize.

Observe readings under Specific Conductance or Conductivity and when they show no significant change for approximately 30 seconds press Enter. The screen will indicate that the calibration has been accepted and prompt you to press any key to return to the Calibrate menu.

Rinse the sensors with DI water between changes of calibration solutions.

After calibration procedure is complete, press any key, as instructed on the screen, to return to the Calibrate menu.

Rinse the sonde in cool tap water and gently dry the sonde. Be very careful not to touch the membrane on the DO probe.

Note: The following table shows several potassium chloride solutions and their specific conductance values.

KCL Molar Concentration	Specific Conductance in (ms/cm)
0.5M	58.64
0.1M	12.90
0.05M	6.668
0.01M	1.413
0.005M	0.718
0.001M	0.147

F) Depth

Note: Depth can be calibrated by zero in the air, at or near the surface of the water to be sampled, do not submerge the sonde.

Select 4. Depth to access the depth calibration procedure. Input 0.00 or some known sensor offset in feet. Press Enter and monitor the stabilization of the depth readings with time. When no significant change occurs for approximately 30 seconds, press Enter to confirm the calibration and zero the sensor with regard to current barometric pressure.

The sensor is not vented; changes in barometric pressure after initial calibration will appear as changes in depth. This is a significant effect, particularly for the 0-30ft option of the depth probe. For Example, a change of 1mm Hg in barometric pressure will change the apparent depth by approximately 0.04 ft.

After depth is zeroed, press any key, as instructed on the screen, to return to the Calibration menu.

Note: The sensors are now calibrated. Press ESC until the sonde Main menu is displayed.

G) YSI 600UPG field set-up and operation

The basic YSI 600UPG consists of the display unit, the data cable, the sonde, and the battery pack. If additional weight is needed, the lead weight can be attached to the nylon line.

H) Preparation for use

Interconnect the display unit, battery pack, sonde, and data cable. Coil cable and keep it kink-free.

Remove the storage cap from the Sonde. Connect the two ends of the data cable to the probe and display unit. Ensure that probe is attached to the data cable with the pin and clip ring.

Ensure that the sponge located in the storage cap is saturated with water so that the sensors will maintain moist. Store the sonde with the damp sponge and cap.

Turn the display unit switch to OFF.

I) Field Set-up and Operation

Note: YSI 600UPG must be precalibrated and the operation checks must be performed prior to using it in the field.

While the unit is in operation aboard the vessel, the boat operator must maintain the boat's position and orientation with wind and tide movement to ensure that the Sonde hangs as vertically as possible.

While the unit is in the operation aboard the vessel, keep the probe away from the engine's propeller to ensure the safety of the Sonde and data cable, and to prevent interference from the propeller wash with all water quality measurements.

Remove unit from storage.

Remove the storage cup from the Sonde. Caution should be taken to avoid any contact with the sensors.

Connect the two ends of the data cable. – Ensure that the probe is attached to the data cable with the pin and clip ring.

Calibrate depth. – At the station above the surface water, press the depth key.

Lower the Sonde to 0.3 meter, for a surface measurement. Wait for thermal equilibrium. Allow thermal equilibrium and then verify that the dissolved oxygen reading is stable. The D.O. sensor is the slowest of all Sonde sensors to match its temperature to that of the water, therefore, after its reading has stabilized, it is time to read all of the required parameters.

Lower the Sonde with cable and weighted nylon line (if utilized) through the water column. Record parameter readings at each meter in depth. Each of the following parameters should be viewed and recorded off of the display unit: temperature, specific conductance, and depth. Record D.O. value last.

Upon reaching the bottom, turn the display unit off and retrieve the Sonde. At the end of the day put the storage cap back on the Sonde and place the unit in its storage bag in the vehicle. This will allow the Sonde to equilibrate quicker for postcalibration of the parameters.

J) YSI 600UPG Postcalibration

Note: Perform postcalibration before clean up and sensor servicing. When performing the postcalibration of the system, it is extremely important that the room temperature, sonde temperature, DI water temperature, and all standard solutions are at thermal equilibrium. If thermal equilibrium needs long time or postcalibration values are outside the QC criteria, postcalibration on the next day is recommended.

a) Dissolved Oxygen

Follow procedures described in section C

Record the data on the logbook. Compare the Saturated DO values from the chart and the instrument values as recorded in the logbook. If the difference between the two is less than 0.5 mg/L the instrument is in calibration. If the difference between the Saturated DO value and the instrument indicates that the instrument is not in calibration, check again the next morning to make sure that the temperature was properly equilibrated. If the difference is still greater than or equal to 0.5 mg/L the data collected during the sampling event is suspect and will be removed from the database by the QA officer. Additionally, the instrument should not be utilized until more extensive cleaning/maintenance is conducted and the instrument calibrates well.

b) Specific Conductance

Follow procedures described in section D

Record the data on the logbook. Compare the displayed value to the saturated oxygen value. If the difference is ≤ 0.5 ms/cm for the 12.89 standard, ≤ 1.0 ms/cm for the 58.6 standard, ≤ 0.017 ms/cm for 1.413 standard or ≤ 0.02 ms/cm for the 0.147 standard the instrument is in calibration. If the instrument is not in calibration, check again the next morning to make sure that the temperature was properly equilibrated. If the difference is still ≥ 0.5 ms/cm for 12.89 standard, ≥ 1.0 ms/cm for the 58.6 standard, ≥ 0.017 ms/cm for 1.413 standard, or ≥ 0.02 ms/cm for the 0.147 standard the data is suspect and will be removed from the database by the QA officer. Additionally, the Hydrolab should not be utilized for that parameter until it has an extensive cleaning/maintenance.

c) Depth

Allow the sonde to be exposed to the air. Determine the depth from the display. Record it on the logbook.

If they differ 0.3 meters from 0.0, the depth is in calibration.

The sonde is now post calibrated.

Store with protective cover and saturated sponge to maintain probe moisture.

Maintenance

L.1) 6030 DO/COND/TEMP PROBES

DO sensor maintenance is usually required when calibration becomes impossible or when the membrane covering the cell becomes wrinkled, bubbled, torn, dirty or otherwise damaged. Follow a regular schedule for membrane replacement. The manufacture suggests membrane replacements prior to each sonde deployment for best results.

If either or both of the silver electrodes are black in color, the manufacturer suggest resurfacing the probe with the sanding disc provided in the reconditioning kit, following corresponding instructions, also found in the kit.

To install a new membrane: Remove the o-ring securing the membrane. Shake out the odd electrolyte.

Rinse the sensor cavity with analyte free water. Refill with fresh D.O. electrolyte (2M KCL) until a perceptible meniscus of electrolyte forms above the entire electrode surface of the sensor. To remove any bubbles trapped in the electrolyte, tap gently, on the side of the D.O. sensor.

To replace the membrane, hold both ends of the membrane with both hands between your thumbs and index fingers. Hold the membrane above the top and carefully drop the membrane over the top of the sensor.

Place the new o-ring over the gold cathode. Do not use any type of grease on the o-ring. Secure the membrane with the o-ring by pushing down with your thumbs on both side of the o-ring. Carefully trim the excess membrane extending below the o-ring.

Allow the membrane to soak overnight in tap water before calibration.

Conductivity- The openings which allow fluid access to the electrodes must be regularly cleaned. Dip a small cleaning brush into clean water and repeatedly insert into each hole. If deposits have formed on the electrode, it may be necessary to use a mild detergent

L.2) Temperature Sensor

Other than assuring a clean probe (no barnacles or other deposits), the temperature sensor does not require any maintenance.

L.3) Depth Sensors

Depth sensors are factory installed, and are located inside the sonde body. Check to insure that the plastic fitting protects the threads of the probe port, be sure to clear any obstructions that may clog the port.

In-Situ Multi-parameter Troll 9000 with Pocket Situ

A) General procedures for calibration

- 1) Perform the calibration and postcheck calibration procedures each day of the instrument is used.
- 2) Maintain a calibration logsheet in which all data pertaining to each precalibration, postcheck calibration or maintenance procedures are entered.
- 3) The calibration should reproduce anticipated field conditions as closely as possible, especially temperature. It is best to calibrate at the temperature that the sensor will be measuring.
- 4) The calibration cup's fill lines indicate the recommended amount of solution for most calibration, and ensure the temperature sensor is immersed. With a full complement of sensors installed, use the lower line as a guide. Except for the 100% dissolved oxygen calibration, the temperature sensor should be immersed in about an inch of fluid.
- 5) First rinse the sensors with tap water, then with distilled or analyte water followed by a rinse with the solution to be used for calibration.
- 6) There are three calibration status indicators. 1) Unstable: indicates the sensor response does not meet the criteria for a valid calibration point. 2) Nominal: indicates the sensor deviation meets early stabilization criteria. 3) Stable: displays when the readings have stabilized sufficiently to take a valid calibration point. The calibration proceeds automatically to the next screen.
- 7) Each time a sensor is calibrated, the information is written to the sensor, where it is stored until the next calibration.
- 8) After a certain amount of use the instrument will not be able to accurately calculate the calibration coefficients. The slope will gradually become lower and lower. At this point the sensor should be replaced.

B) Calibration

a) Specific Conductance

- 1) Remove the black PVC end cap from the calibration cup and screw the top of the stirrer to the bottom of the calibration cup.

- 2) Fill the calibration cup to the lowest fill line with solution.
- 3) Select MP TROLL 9000 in the navigation tree.
- 4) Select conductivity in the parameter list.
- 5) Select calibrate.
- 6) Select the calibration solution the sensor is soaking in. If the calibration solution concentration is not in the selection. Select other and enter the specific conductance of the solution in $\mu\text{S}/\text{cm}$.
- 7) Select next to continue.
- 8) In the next screen, select run to begin the stabilization.
- 9) When the sensor reaches the stable stage, the display unit will move to the final screen showing the new cell constant as calculated for the selected range during the calibration process.
- 10) Select finish to program the sensor with the displayed cell constant. The Kcell constant should range between 0.33-0.43. If the constant is out of the specified range check the sensor for fouling of the electrode.
- 11) Record the calibration conductivity value in the calibration logsheet.
- 12) The conductivity sensor is now calibrated and ready to use in the range for which it was calibrated.

b) PH

- 1) Rinse the calibration cup with tap water, followed by distilled or analyte free water and first pH standard to be calibrated.
- 2) Fill calibration cup (with stirrer attached) with the standard solution to the lowest fill line.
- 3) Select MP TROLL 9000 in the navigation tree.
- 4) Select pH in the parameter list.
- 5) Select calibrate.
- 6) Select the number of calibration points for this calibration, and the pH value of the calibration solution for each point. Since the range of pH encountered in the field may be unknown. A three point calibration is recommended.
- 7) Select next to continue.
- 8) Select run to begin the stabilization.
- 9) The wizard returns to the previous screen and waits for you to situate the probe in the next calibration solution.
- 10) Remove the calibration cup, discard the solution, rinse the calibration cup with tap, analyte free water and the next standard solution. Refill the calibration cup with the next solution and attach it to the instrument.
- 11) Select run to begin the stabilization for the second calibration point.
- 12) Repeat step 9 and 10 for the third calibration point.
- 13) The final screen shows the sensor slope and offset calculated during the calibration process. For a 3-point calibration, two sets of calculated coefficients will be shown.
- 14) Offsets calculated by the software for pH 7 will typically be between 390-450 mV. If the offset falls far outside these limits, it may be time to replace the sensor. The calculated slope will be typically between $-54\text{mv}/\text{pH}$ and $-62\text{mv}/\text{pH}$. A

calculated slope greater than -50mv/pH or less than -66mv/pH may indicate the sensor needs replacing.

- 15) Select finish to program the sensor with the newly calculated calibration coefficients.
- 16) Record the pH 4,7,10 calibration values, the offsets and slopes on the calibration logsheet.
- 17) The pH sensor is now calibrated and ready to use.

c) Dissolved Oxygen

- 1) Invert the TROLL so the DO sensor faces upward.
- 2) Fill the calibration cup (without stirrer attached) with water to just below the DO membrane.
- 3) Use soft swab or the corner of a tissue to remove moisture from the membrane.
- 4) Reattach the end cap loosely to insure the chamber is not pressurized. For proper venting, loosen the end cap until the small hole in the treads near the o-ring is at least partially visible.
- 5) Select the TROLL 9000 in the navigation tree.
- 6) Select Dissolved Oxygen in the parameters list.
- 7) Select calibrate.
- 8) If the instrument has a vented cable choose used vented cable. Click OK to proceed.
- 9) Select continuous mode and one point calibration.
- 10) Click next to continue.
- 11) Select run to begin the stabilization for 100% DO calibration point.
- 12) The final screen shows the sensor slope and offset calculated during the calibration process. The slope of a properly functioning sensor should be between 35 and 75 nA/(mg/l). If the slope is slightly outside this range, repeat the calibration. The sensor may require further conditioning. Sensors that repeatedly fall outside this range may require a new membrane. The default offset for a one-point calibration is 2nA. Offsets for two-point calibrations should be less than 10 nA.
- 13) Select finish to program the sensor with the newly calculated calibration coefficients.
- 14) Record saturated DO from table, calibration DO and the DO slope on the logsheet.
- 15) The DO sensor is now calibrated and ready to use.

d) Temperature

Central office personnel will conduct temperature checks for multiprobes against an NIST certified thermometer annually when conducting site visits.

The temperature function for the In-Situ is set at the factory and can not be calibrated and corrected in the field. There is no field calibration procedure for temperature but rather a QC check to verify the instrument is functioning properly. Regions should check the temperature probe against another multiprobe instrument's temperature probe semi-annually. If a discrepancy should occur (temperatures are not $\pm 1^\circ\text{C}$) contact Central office so that the

probes can be checked against an NIST certified thermometer soon as possible. If there is good agreement between the instruments, then Central office personnel will check the instruments against an NIST certified thermometer as planned. The temperature check should be conducted in an ice/water mixture (e.g. 4 °C) and at a warm water temperature that will best approximate the highest ambient temperature expected to be sampled (e.g. 25-30 °C) where the probe(s) and/or NIST certified thermometer are lowered into the mixtures simultaneously and read. Send the In-Situ unit back to the manufacturer for temperature calibration if the thermometer and In-Situ values differ more than 1 °C

C) Set up

- 1) If the short calibration cable is used for calibration, switch the cable to utilized in the field.
- 2) Remove the storage cup from TROLL, screw on the restrictor and store the sensor in a moist environment when not in use.

D) Profiling

- 1) At the station, turn on the IPQA.
- 2) Select MP TROLL 9000 in the navigation tree.
- 3) Select parameters in the navigation tree.
- 4) Select profiler to start the profiler.
- 5) After a moment, each active channel will be read sequentially, and the reading will be displayed. Readings are updated approximately every two seconds as the profiler cycles through the available channels in turn. The currently selected measurement unit is shown below each reading.
- 6) When you are ready to exit the profiler, click close. The parameter view will return to the screen.

E) Logging profiler data

To log a single set of profiler readings, click or tag the snapshot button in the view. The snapshot button flashes when logging. When it is done, it returns to not logging status.

F) Retrieving logged profile data

- 1) Expand the data folder in the navigation tree by tapping the +.
- 2) Expand the node for the device type and serial number.
- 3) Look for the data file named with date and time of the profiler reading.

G) Postcheck Calibration

The postcheck calibration should be performed at the end of the run either in the office or in the field. Do not calibrate the instrument to the standard values during postcheck calibration procedure. A properly maintained instrument that is used on a regular basis should remain fairly stable and free from marked drift or variation in its measurements. Postcheck calibration of the instrument

provides the user with immediate feedback on the instrument's general reliability and a written performance record for each of the parameters. Based on years of data, the following ranges are considered acceptable in day-to day instrument drift.

Dissolved Oxygen	±0.5mg/l
PH	±0.2 units
Conductivity(56.8)	±1.0ms/cm
Conductivity(12.89)	±0.5ms/cm
Conductivity(1.413)	±0.017ms/cm
Conductivity(0.147)	±0.02ms/cm

These ranges take into consideration real-world factors which a Unit is typically exposed to during the rigors of a day in the field (e.g. temperature extremes, rough rides in a truck etc.). Usually, a well-maintained instrument will remain demonstrate tighter agreement than the ranges listed. Performance that falls outside of the acceptable ranges indicates the unit needs maintenance focused on the specific parameter that falls outside its range. If the performance remains substandard, the unit should be removed from service until it is repaired. It is highly advisable to have a backup unit available. The data collected during the sampling event is suspect and should not be keyed into the database or removed from the database.

H) Maintenance

- a) Removing sensors: Sensors may be removed for inspection, cleaning, routine maintenance and storage. Remove a sensor by positioning the yoke of the sensor removal tool at the point where the sensor enters the sensor block. Firmly pry the sensor upward until it pops out.
- b) Installing sensors
 - 1) Check lubrication of the sensor o-rings. The sensor o-ring requires generous lubrication before installation. If the o-ring appears dry, apply a silicone lubricant before installing.
 - 2) Align the mark on the sensor with the alignment mark on the correct port.
 - 3) Press the sensor with sensor insertion tool firmly into the port until it is securely seated. When properly inserted a gap of about 0.06" (width of the sensor removal tool) remains between the widest part of the sensor and the instrument body, for ease of the sensor removal.
- c) pH sensor:

If a film develops on the glass electrode, the sensor response will tend to be sluggish. A deposit on the junction will result in an erratic response. In these cases, rinse the sensor in a detergent solution, then a rinse it in deionized water, and soak it in pH 4.00 buffer. This should restore the response. If not, sensor response may be restored by soaking in 0.1M HCL solution, followed by thoroughly rinsing. Soak the sensor in 2M KCL for at least an hour before calibration.

If the sensor glass should become dehydrated, performance can often be restored by soaking the sensor for at least an hour in pH 4.0 buffer or 2 M KCL . Check the reading after soaking for an hour or so. If the response has not improved, try soaking the sensor overnight and test again. If the response has still not improved, the sensor should probably be replaced.

d) Conductivity sensor:

Check the sensor for fouling of the electrodes. If necessary, flush the sensor with water, or swish in a mild detergent solution and rinse with tap water. A swab or soft bristle brush may be used to gently clean the electrodes. Remember that electrodes are made of graphite, which is soft and easily damaged.

e) Dissolved Oxygen sensor:

Inspect the sensor and membrane if readings begin to drift.

- ◆ Check for discoloration of electrodes due to silver chloride deposition.
- ◆ Inspect the membrane for integrity of the surface, for the presence of algal growth or other contaminants, for crystallization that may indicate a leak in the membrane, and to ensure there no air bubbles are trapped under the membrane.

Cleaning the electrodes:

Remove the membrane module and clean the electrodes as follows:

Cathode: use a polishing strip to buff the platinum cathode until it is shiny. This removes any deposits, increasing the chemically active surface of the electrode for a stronger DO signal.

Anode: remove silver chloride deposits from silver anode by cleaning with a soft bristle brush and ammonia. Excessive discoloration may be removed more easily by soaking for a half-hour in ammonia before cleaning with the brush. The surface of anode should appear uniform but not necessarily shiny. Regular cleaning will prevent pitting of the anode surface, caused by accumulated silver chloride deposition. Severe pitting can not be removed, the sole remedy is to replace the sensor. After cleaning, rinse thoroughly in analyte free water and shake dry.

Replacing the membrane module:

- 1) Remove the sensor from the instrument. Remove and discard the used membrane module. Inspect and clean the sensor as needed.
- 2) Remove the soft protective cap from a new DO membrane module.
- 3) Holding the membrane module open-end up slowly fill the cap with electrolyte. Try to eliminate all air bubbles in the electrolyte –filled

membrane module by tapping the side of the cap briskly with your fingernail.

- 4) Insert the clean DO sensor into the open end of the membrane module. To minimize the introduction of air, allow some of the electrolyte to overflow from the open end as the sensor is inserted. Ensure the membrane does not leak. You should not see any drops on the surface. When properly assembled, the membrane will bulge out slightly. There should be no visible air bubbles.
- 5) Thread the membrane module to the DO sensor.
- 6) Install and condition the sensor. Remember to condition the sensor at least overnight in continuous mode before recalibrating with a new membrane. Even with all visible air bubbles removed, a certain amount of gas will be trapped under the membrane. The conditioning period will remove this excess oxygen.

Section V: Dissolved Oxygen Method (Winkler Azide Modification Titration)

A) Applicability:

This procedure is applicable to the analysis of dissolved oxygen in fresh, estuarine and coastal water samples. The results are measured and reported as mg dissolved oxygen /L of water.

B) Summary of method:

The iodometric test is the most precise and reliable titrimetric procedure for DO analysis. It is based on the addition of divalent manganese solution, followed by a strong alkali, to the sample in a glass-stoppered bottle. Dissolved Oxygen (DO) rapidly oxidizes an equivalent amount of dispersed divalent manganous hydroxide precipitate to hydroxides of higher valence states. In the presence of iodide ions in an acidic solution, The oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent to the original DO content. The iodine is then titrated with a standard solution of Phenylarsine Oxide.

C) Health and Safety Warnings:

- 1) It is important to wash your hands after handling laboratory chemicals. While some laboratory chemicals are not dangerous, many those used with the Winkler method are poisonous or harmful to skin and clothing or both.
- 2) Rubber gloves and safety glasses should be used.

D) Cautions

Winkler titrations need to be conducted within 8 hours of fixing the sample. Samples should be fixed on site and stored in a box.

E) Interference:

- 1) There are a number of agents that may cause interference to the Winkler dissolved oxygen test, including iron salts, organic matter, excessive suspended matter, sulfide, sulfur dioxide, residual chlorine, chromium, cyanide and certain oxidizing and reducing agents.
- 2) Various modifications of the original Winkler procedure for DO have been developed to compensate for or eliminate interference. The Azide modification is for sample containing nitrate ions and ferrous irons.

F) Apparatus and Material:

a) Equipment

Digital Buret

300 ml glass stopper BOD bottle

250 ml wide-mouthed Erlenmeyer flasks

200 ml volumetric flask

Stirbar and stirbar retriever

Magnetic stirplate

b) Chemical

Hach Manganese Sulfate powder pillow

Hach Alkali-iodide-azide powder pillow

Hach Sulfamic acid powder pillow

Starch indicator solution

Phenylarsine Oxide 0.025N

Note: PAO is very poisonous. Care must be taken in handling this reagent.

G) Instrument or Method Calibration

The digital buret should be calibrated following the manufacture's instructions.

H) Sample Collection:

a) Collecting a Winkler sample via the Pump and hose procedure:

- 1) Attach a piece of PVC pipe, which has a copper tube in the middle, to the end of hose.
- 2) Attach a piece of plastic tubing to the copper tube. The plastic tubing should be long enough to reach to the bottom of the BOD bottle

- 3) Rinse the BOD sample bottle 1-2 times with sample water discarding the rinse each time.
- 4) Fill the BOD bottle using a slow rate of flow. Slowly turn the BOD bottle to an upright position, keeping the plastic tubing submerged at all times. If any bubbles are observed while filling the bottle, start over again.
- 5) Fill the sample to overflow the bottle by approximately 25-50 ml
- 6) Immediately perform steps 1 through 5 in section I.

b) Collecting Winkler samples via the bucket procedure

- 1) Rinse the BOD bottle 1 or 2 times with sample, discarding the rinse.
- 2) Fill the BOD bottle with sample holding the bottle horizontally to avoid introducing air bubbles into the BOD bottle.
- 3) Immediately perform steps 1 through 5 in section I.

I) Handling and Preservation

- 1) Immediately add 1 pillow of Manganese Chloride powder, followed by 1 pillow of alkali-iodide-azide powder
- 2) Place the glass stopper onto the sample bottle carefully to avoid introducing air bubbles.
- 3) Invert the sample bottle until the sample appears to be homogeneous. This must be done immediately after sample is collected.
- 4) When the precipitate has settled to at least half the sample bottle volume (leaving clear supernatant above the manganese hydroxide floc), mix the sample again by inverting the bottle until the sample appears to be homogeneous.
- 5) Samples stored at this stage should be protected from strong sunlight and titrated as soon as possible but no later than 8 hours after fixing.

J) Sample Bottle Cleaning:

- 1) Sample containers must be clean, dry and free of contaminants. Using a lab grade detergent, wash with a good cleaning brush and rinse thoroughly with tap water followed by analyte-free water. Allow the bottle to dry in an upside-down position.

- 2) All sample containers should be cleaned immediately after the test has been completed to prevent accumulation of residues in the containers, which can effect the test.

K) Sample Analysis:

- 1) The titration must be completed within 8 hours of fixing the sample.
- 2) Allow the floc to resettle to at least half the sample bottle.
- 3) Add 1 pillow of Sulfamic acid.
- 4) Place the stopper on the bottle and shake well until the precipitate has dissolved. Occasionally, a dark brown precipitate persists in the bottle after acidification. This precipitate will dissolve if the solution is kept for a few minutes longer than usual.
- 5) Pour 200 ml of the sample from the BOD bottle into a 200 ml volumetric flask and transfer to an Erlenmeyer flask.
- 6) Titrate with 0.025N Phenylarsin Oxide (PAO) until the solution is a pale yellow (straw) color. Add a small quantity of starch indicator.
- 7) Titrate with 0.025N PAO until the blue color disappears. Record the total number of ml of PAO used in the calibration logsheet.

L) Data Calculation:

Calculate the concentration of DO in the sample using the following formula:

$$\text{MI/L DO} = \frac{\text{ml titrant} \times \text{Normality of titrant} \times 8000}{\text{Equivalent volume of sample titrated}}$$

If the normality of the titrant is exactly 0.025N and the equivalent volume of 200 ml of sample is titrated, the amount of oxygen dissolved in the original sample will be equal the number of ml of PAO used in the titration.

M) Data Management and Record Management

All records must be maintained in the logsheet and keyed into CEDS.

N) Quality Control and Quality Assurance

- 1) A Winkler titration should be preformed for every 25 sites sampled (4%) to confirm probe method accuracy.

- 2) If the probe method DO concentration disagrees with the results of the Winkler titration method by ± 0.6 mg/l, all the DO data collected since the previous Winkler titration with that probe instrument will be flagged.

M. Corrective Action

- 1) If the difference is ± 0.6 mg/l most likely the membrane and electrolyte solution need to be changed. Change the membrane and electrolyte solution, recording the date of change on the maintenance sheet. Collect a Winkler sample on the next sampling run using that probe. If the difference between Winkler and the probe is less than 0.6mg/l. It means the problem has been resolved.

O) Reference:

Standard Methods for the examination of water and wastewater, 18th edition.

Section VI: Sample Identification and Corrective Action

A) Field Data Sheet:

A field data sheet is required to be carried in the field by the sampler for each run. Make entries in the field data sheet for all the field parameters.

B) Sample label and tag

The sampler should print the label from the pre-print label file in the computer. The label should have the following information: station ID, date collected, time collected, depth, unit code, collector, group code, preservative, lab processing code, blank/dup designation, priority and container number. The preprinted label should have filled in all the information except the collected time based on the monthly run information in CEDS. The collector fills the time in the field using indelible ink pen. The Avery label should be placed on the plastic or glass sample bottles or placed on a label that is then attached to the sample containers. When using cubitainers the label needs to be placed on the sample tag that is then attached to the containers.

C) Corrective Action

For the corrective action plan to be operative, all personnel associated with the program must report any suspected deficiencies in procedures or equipment. This is especially important for DEQ field personnel and DCLS lab personnel. Identification and correction of the problems in sample collection, preservation, handling and analysis is essential for an effective program.

The corrective action request (CAR) form (see Appendix C) is used to document the problem and steps taken for correction. CAR forms may originate in regions, central office or DCLS.

The originator:

- 1) Identifies the problem.
- 2) List possible causes (if known)
- 3) Notes the date the problem was identified
- 4) Identifies samples or field data that may be invalid as a result of the problem
- 5) May recommend corrective action

CAR forms that originate in the region or central office are forwarded to the appropriate QA officer for review and recommendations. The QA officer forwards the form to the appropriate supervisor for review, recommendations and a final decision on appropriate corrective action. After resolution of the problem, the supervisor provides copies of the completed form to appropriate personnel on his staff and central office QA/QC officer. The supervisor has the responsibility for implementation of this corrective action. The

QA/QC staff in central office may provide additional comments or recommendations to the supervisor for his review if requested.

CAR forms that originate in DCLS are forwarded to the central office QA officer for review, recommendations or concurrence. Then, if appropriate, these forms are forwarded to the appropriate supervisor for a final decision and implementation.

It is the responsibility of the originator to notify management and the QA officer in central office if the corrective action system is not operating effectively. In this situation, the originator may elect to call or send a CAR form directly to QA/QC central.

Appendix A.....Calibration Logsheet

Instrument Calibrations and Post Calibartion Logsheet

Meter # _____

Cal.Type	Date	Time	Tmep.	Press. (mm Hg.)	Theor. (chart) DO	Meter initial DO	Meter Cal. DO	pH 7 init./ calib.	pH 4 or 10 init./ calib.	Cond. Init./ calib.	Batt. Volt.	Init./ Run ID
Pre												
Post												
Pre												
Post												
Pre												
Post												
Pre												
Post												
Pre												
Post												

Appendix B.....Saturated Dissolved Oxygen Chart

Temp in °C	O ₂ concentrations in mg/l									
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
5	12.75	12.71	12.68	12.65	12.61	12.58	12.55	12.52	12.48	12.45
6	12.42	12.39	12.36	12.32	12.29	12.26	12.23	12.20	12.17	12.14
7	12.11	12.08	12.05	12.02	11.99	11.96	11.93	11.90	11.87	11.84
8	11.81	11.78	11.75	11.72	11.69	11.67	11.64	11.61	11.58	11.55
9	11.53	11.50	11.47	11.44	11.42	11.39	11.36	11.33	11.31	11.28
10	11.25	11.23	11.20	11.18	11.15	11.12	11.10	11.07	11.05	11.02
11	10.99	10.97	10.94	10.92	10.89	10.87	10.84	10.82	10.79	10.77
12	10.75	10.72	10.70	10.67	10.65	10.63	10.60	10.58	10.55	10.53
13	10.51	10.48	10.46	10.44	10.41	10.39	10.37	10.35	10.32	10.30
14	10.28	10.26	10.23	10.21	10.19	10.17	10.15	10.12	10.10	10.08
15	10.06	10.04	10.02	9.99	9.97	9.95	9.93	9.91	9.89	9.87
16	9.85	9.83	9.81	9.79	9.76	9.74	9.72	9.70	9.68	9.66
17	9.64	9.62	9.60	9.58	9.56	9.50	9.53	9.51	9.49	9.47
18	9.45	9.43	9.41	9.39	9.37	9.35	9.33	9.31	9.30	9.28
19	9.26	9.24	9.22	9.20	9.19	9.17	9.15	9.13	9.11	9.09
20	9.08	9.06	9.04	9.02	9.01	8.99	8.97	8.95	8.94	8.92
21	8.90	8.88	8.87	8.85	8.83	8.82	8.80	8.78	8.76	8.75
22	8.73	8.71	8.70	8.68	8.66	8.65	8.63	8.62	8.60	8.58
23	8.57	8.55	8.53	8.52	8.50	8.49	8.47	8.47	8.44	8.42
24	8.41	8.39	8.38	8.36	8.35	8.33	8.32	8.30	8.28	8.27
25	8.25	8.24	8.22	8.21	8.19	8.18	8.16	8.15	8.14	8.12
26	8.11	8.09	8.08	8.06	8.05	8.03	8.02	8.00	7.99	7.98
27	7.96	7.95	7.93	7.92	7.90	7.89	7.88	7.86	7.85	7.83
28	7.82	7.81	7.79	7.78	7.77	7.75	7.75	7.73	7.71	7.70
29	7.69	7.67	7.66	7.65	7.63	7.62	7.61	7.59	7.58	7.57
30	7.55	7.53	7.53	7.51	7.50	7.49	7.48	7.46	7.45	7.44

Barometric Pressure Correction factor:

Conversion of inches Hg to mm Hg: use 25.4 as

factor.

mm Hg.	Corr.Factor	mm Hg.	Corr.Factor	mm Hg	Corr.Factor	mm Hg	Corr.Factor
775	1.02	750-746	0.987	725-721	0.953	700-696	0.92
770-766	1.014	745-741	0.98	720-716	0.947	695-691	0.914
765-761	1.007	740-736	0.973	715-711	0.94	690-686	0.907
760-756	1.0	735-731	0.967	710-706	0.934	685-681	0.90
755-751	0.993	730-726	0.96	705-701	0.927	680-676	0.893

Appendix C.....Corrective Action Request Form

Section I: to be completed by originator

Date:

Submitted By:

A. Nature of Problem:

B. Possible Cause:

C. Date of Problem Identified:

D. Samples That May Be Invalid:

E. Recommended Corrective Action (Optional):

Section II: to be completed by program manager

Date:

Name:

A. Recommended Corrective Action:

B. Follow Up Action Required:

C. Implementation Will Begin On:

Section III: to be completed by QA Officer

Date:

A. Recommended Corrective Action:

B. Follow Up Action Required:

C. Implementation Will Begin On:

Appendix D.....Entering QA/QC into CEDS

QA/QC Run IDs:

QA/QC run IDs consists of the first letter of the region conducting the sampling followed by the letters QA and 2-letter program code under which the samples are collected (e.g. TQAAQ for Tidewater regional QA run for Ambient Monitoring Program).

Blank/Dups designations:

R- Regular sample (default designation)

EB- Equipment Blank

S1- First subsample of a field split sample (these data are stored in the regular run ID)

S2- Second subsample of a field split sample (these data are stored in the QA/QC run IDs)

Container number designations:

1- 9 S1 sample containers

11 – 19 S2 sample containers (the ones place of a S2 container is the same as the corresponding S1 container e.g. if S1 for NUT4 is container number is 2 then S2 for NUT4 is container number is 12).

21 – 29 Equipment blanks (the ones place for equipment blanks also correspond to the S1 containers for the sample types e.g. S1 for NUT4 is 2 then EB for NUT4 is 22.)

Lab Process code designations:

D- indicates to the lab to perform lab splits on the sample

M - indicates to the lab to perform matrix spikes on the sample

Year run schedule:

- 1) In CEDS click on application/environmental monitoring/water/yearly run schedule.
- 2) In the yearly run schedule set up a generic QA/QC run ID (e.g.TQAAQ)
- 3) Use QA as the station ID and survey program.
- 4) Enter the lab Proc Code for NUT4 and TNTUL containers as M.
- 5) Enter the appropriate depths (0 for EB), container IDs, parameter group codes and save. Once this is completed, the QA/QC run ID can be used for all QA sampling events.

Monthly schedule:

- 1) Click on application/environmental monitoring/monthly run schedule
- 2) Click on the get yearly run data tab
- 3) Enter the regular run ID and the date to be collected on the first line of pop-up screen. On the next line enter the QA/QC run ID (e.g. TQAAQ and the date to be collected)
- 4) Click on the get yearly run data button. The database will be automatically updated with the runs chosen and will be displayed in the monthly run schedule screen. Save.
- 5) Click on the query button.
- 6) Enter the regular run ID, the station chosen for QA/QC and the date as scheduled in step 5.
- 7) Change the blank/dups designation for all containers to S1
- 8) Save
- 9) Click the query button
- 10) Enter the QA/QC run ID (TQAAQ) and the date scheduled in step 3
- 11) Change the station ID from QA to the name of the station chosen for QA/QC sampling for all samples
- 12) Change the blank/dup designation for all containers numbered 11-16 to S2
- 13) Change the blank/dup designation for all containers numbered 21-26 to EB
- 14) Save the information and exit CEDS

Appendix E.....Miscellaneous Special Sampling Procedures

a. Cyanide

To minimize loss of cyanide due to vaporization of CN^- , the sample must be adjusted to pH 12 or more with NaOH after testing for interferences or oxidizers. The sample matrix may promote rapid loss of cyanide due to volatilization if the pH is less than 10; the sample pH must be 12 or more to hold HCN in solution and ensure representative samples.

1. Total Cyanide

- 1) As a general rule, if residual chlorine is present in the sample, sulfide will not be present. If sulfide is present, residual chlorine will not be present.
- 2) If the sample contains residual chlorine, add 0.6 g. ascorbic acid per liter of sample volume.
- 3) Maximum holding time is 24 hours when sulfide is present.
- 4) To extend the holding time requirement, samples may be tested with lead acetate paper premoistened with acetic acid solution before pH adjustments in order to determine if sulfide is present
- 5) If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is then filtered.
- 6) Sodium hydroxide (NaOH) pellets are then added to raise the pH to 12. This can be achieved by adding a premeasured amount of NaOH to the sample - then test the sample with a pH strip and continue to add NaOH pellets until a pH of 12 is achieved.
- 7) Immediately after collection and pH adjustment, samples shall be cooled to 4°C in an ice chest.

2. Free Cyanide

- 1) To minimize CN^- losses due to vaporization, the pH of the sample must be adjusted to 12 or more with NaOH.
- 2) This pH adjustment can be achieved by adding a premeasured amount of NaOH to the sample and then test drop by drop until a pH of 12 or more is achieved.
- 3) Immediately after collection and pH adjustment, samples should be cooled to 4°C in an ice chest.
- 4) Free cyanide samples should be exposed to light as little as possible to prevent hexacyanoferrate breakdown.

b. Sulfide

- 1) Collect sample with minimum aeration in a one quart cubitainer.
- 2) Add 40 drops of 2N zinc acetate solution (4 drops of 2N zinc acetate solution per 100 ml sample).
- 3) Add NaOH pellets to raise the pH to 9.
- 4) Fill Bottle completely, cap container and place in an ice chest.

c. Pesticides and Herbicides

- 1) Samples to be analyzed for herbicides/pesticides must be in the pH range of 5 to 9. This pH adjustment may be performed upon receipt at DCLS and may be omitted if the samples are extracted within 72 hours of collection.

A note should be made on the sample tag for the lab to check the pH of the sample.

- 2) For the analysis of aldrin, add 80 mg/l sodium thiosulfate to the water sample in the sample bottle when residual chlorine is present.
- 3) Immediately after collection and the addition of sodium thiosulfate, sample shall be cooled to 4⁰ C in an ice chest.

d. Purgeable (Volatile) Organic and Aromatic Compounds**Purgeable Organic Compounds (Volatiles)**

- 1) If the sample contains residual chlorine, add 0.008% sodium thiosulfate preservative (10mg/40 ml is sufficient for up to 5 ppm CL₂) to the empty sample vial just prior to transport to the sampling site or at the sampling site.
- 2) Collect sample in a clean 500 ml stainless steel beaker. Fill two 40 ml sample vials to a positive meniscus in such a manner that no air bubbles pass through the sample as the vial is being filled. Seal the vial so that no air bubbles are entrapped in it. Turn the vial upside down to check for air bubbles. Place vials in Styrofoam packing to prevent breakage.
- 3) Immediately after collection, samples shall be cooled to 4⁰ C in an ice chest.
- 4) Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions. Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified and analyzed for these aromatics.
- 5) A travelling blank (trip blank) must accompany all volatile organic samples. The trip blank should be prepared identically as the sample will be prepared, i.e. if 6N HCL is to be added to the sample, then acidify the blank. Add 10 mg sodium thiosulfate if chlorine residual is expected to be present. Fill a 40 ml glass vial with teflon lined septum (acidified if sample is acidified) with analyte free water at the office. Place vial where other sampling vial will be kept throughout the whole sampling process, i.e., it travels with the sampling vial.

e. Base/Neutrals and Acid Extractables (Semivolatiles)

- 1) If the sample contains residual chlorine, add 0.008% sodium thiosulfate (80mg/L) preservative to each of two one liter amber glass bottles and mix well.
- 2) Check pH of sample, if pH value falls outside the range of 6-9, adjust pH accordingly.
- 3) Sample must be stored in the dark.
- 4) Immediately after collection, samples shall be cooled to 4⁰ C in an ice chest.

f. Petroleum Hydrocarbon Identification and Quantitation in Water Samples

- 1) When collecting pure petroleum product from the surface of water, fill one 40 ml glass vial having a teflon lined cap. Exclude as much water as possible from vial. It is not essential to obtain a positive meniscus. Tightly secure cap.
- 2) Refrigerate sample until analysis. Analyze sample within 14 days after collection.
- 3) The analysis of pure product will provide petroleum identification only.

g. Sampling When Pure Product is Not Noticeable

- 1) Collect water samples directly in sample containers whenever possible.
- 2) When visual inspection of sample does not indicate noticeable pure product, but petroleum odors exist, or you are uncertain of either a noticeable product or odor, the following sample containers are needed: one 1/2 pint amber glass jar with teflon lined cap and one 40 ml glass vial with teflon lined septum.
- 3) If the sample cannot be collected directly in the sample container, one can collect the sample in a clean 500 ml stainless steel beaker. Acidify sample with 6 N HCl acid to a $\text{pH} \leq 2$. If sample contains residual chlorine, add 60 mg sodium thiosulfate to 1/2 pint amber glass jar and 10 mg sodium thiosulfate to 40 ml vial prior to adding sample.
- 4) Fill jar and vial slowly with acidified sample so that no air bubbles pass through the sample. Fill vial to a positive meniscus and immediately cap containers. Do NOT remove cap once it is secured. Invert to check for air bubbles. If air bubbles are present, fill another vial and discard old sample and container.
- 5) Refrigerate samples until analysis. Analyze sample within 14 days after collection.

h. Total Petroleum Hydrocarbon (TPH) in Water Samples

TPH analysis is appropriate for kerosene, diesel, or heavier oils.

TPH determinations are more appropriate for soils as follow-up regulatory monitoring or when the nature of petroleum is known (i.e. tank closure).

- 1) Collect water samples directly in sample containers whenever possible.
- 2) Collect one 1/2 pint amber glass jar with teflon lined cap.
- 3) If residual chlorine is present, add 60 mg sodium thiosulfate to the 1/2 pint amber glass jar prior to adding sample.
- 4) Refrigerate sample until analysis. Recommended storage prior to analysis should not exceed 7 days, but federal regulations allow storage up to 14 days.

i. Volatile Aromatic Hydrocarbons Including Benzene, Toluene, Ethyl Benzene and Xylene (BTEX) in Water Samples

Volatile Aromatic Hydrocarbons including BTEX is the appropriate analysis for gasoline.

- 1) Collect sample in a clean 500 ml stainless steel beaker. Acidify sample with 6 N HCl acid to a $\text{pH} \leq 2$. If sample contains residual chlorine, add 10 mg sodium thiosulfate to 40 ml glass vial prior to adding sample.
- 2) Collect sample in replicate. Fill two vials slowly with acidified sample to a positive meniscus. Tightly secure cap. Invert to check for air bubbles. Do NOT unscrew cap on

vial once cap has been secured. Resample with a new vial if air bubbles are present and discard old sample.

j. Toxicity Test Samples

- 1) No preservatives should be added to the sample container. All air should be removed from the container.
- 2) The samples should be immediately iced and maintained at a temperature of 4⁰ C.
- 3) If the sampler must dechlorinate the samples in the field, this must be noted on the chain of custody form with the amount of dechlorinating agent added.
- 4) The sample is transported directly or shipped overnight to OERS laboratory. All samples must be addressed to OERS and should contain the statement: **Deliver Immediately to Laboratory.**
- 5) A sample for toxicity tests must be used for the first time within 36 hours of collection. Exceeding this time limit voids the sample.

k. Sample Handling

- 1) In the ice chest, samples shall be placed upright - i.e. the neck of the sample container shall be above the level of water and ice.
- 2) Ship all samples to the lab as soon as practical (generally the same day as collected).

l. Petroleum Hydrocarbon Identification, Total Petroleum Hydrocarbons and BTEX in Soil samples

- 1) Collect soil sample directly into glass container for surface samples or use a clean stainless steel or teflon scoop.
- 2) Fill half-pint wide mouth glass jar with teflon lined cap. Sample should be protected from light by using an amber jar or wrapping the jar with aluminum foil.
- 3) Refrigerate sample during transport and storage.
- 4) Analyze sample within 14 days after collection.